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Treatment of Aqueous Biomass and Waste via Supercritical Water Gasification for the Production of CH₄ and H₂

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A thesis submitted in partial fulfillment of the requirements for the degree in Master of Engineering Science

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**TREATMENT OF AQUEOUS BIOMASS AND WASTE VIA
SUPERCRITICAL WATER GASIFICATION FOR THE PRODUCTION
OF CH₄ AND H₂**

(Thesis format: Integrated Article)

by

Izad Behnia

Graduate Program in Engineering Science
Chemical Engineering

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Engineering Science

The School of Graduate and Postdoctoral Studies
The University of Western Ontario
London, Ontario, Canada

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Abstract

The present study targets to convert aqueous fraction of fast pyrolysis oil into methane and hydrogen gases via supercritical water gasification (SCWG). Water above its critical point is referred to as supercritical water, which has unique properties such as a loss of hydrogen bonding, becoming an excellent solvent for organic compounds. In this thesis, SCWG was used to gasify slurry materials into high calorific gases including CH₄ and H₂. Production selectivity towards more methane or hydrogen was affectively controlled by operational conditions. However, in the absence of catalyst (bank test), gas formation was very minimal. SCWG of glucose as an organic model compound was studied to screen the best catalyst for methane production. Ni_{20%}Ru_{2%}/γ-Al₂O₃ catalyst was able to convert all carbon in glucose to gases at a temperature of as low as 500 °C and weight-hourly space velocity (WHSV) of 3 h⁻¹. This catalyst significantly promoted methane production and produced 0.5 mol methane per mole of carbon in the glucose feedstock. High stability and activity of this catalyst were observed during 20 hours on stream. It was also found out from this study that nickel loading, temperature, substrate concentration and feeding rate or WHSV greatly affected carbon conversion and yields of CH₄ and H₂ in SCWG. For instance, higher temperatures favor hydrogen formation while lower temperatures promote methane yield. Moreover, the Ni_{20%}Ru_{2%}/γ-Al₂O₃ catalyst demonstrated to be active for gasifying the aqueous fraction of fast pyrolysis oil via SCWG. Besides, the aqueous fraction of pyrolysis oil was gasified to a high extent in the presence of this catalyst, and 0.9 mol/mol of carbon in feedstock (2.98 wt.% C) was converted into CH₄ and CO₂ at 700 °C.

Keywords: supercritical water gasification (SCWG), glucose, aqueous fraction of pyrolysis oil, catalyst screening, nickel catalyst, nickel loading, ruthenium co-catalyst, effects of temperature, effects of WHSV, effects of substrate concentration.

Co-Authorship Statement

Chapters 3 and 4 are article manuscripts which will be submitted to peer reviewed journals. The contribution of each author is stated below.

Book chapter (Springer-Verlag, Berlin, December 2013 (expected)):

Production of CH₄ from biomass via supercritical water gasification (SCWG). In Near-Critical and Supercritical Water and their Applications in Biorefineries; literature review

Authors: Izad Behnia, Zhongshun Yuan, Paul Charpentier, Chunbao (Charles) Xu

Editorial committee: Ed. Zhen Fang and Chunbao (Charles) Xu

Chapter 3:

Screening of metallic catalysts and supports for methane and hydrogen production from glucose via supercritical water gasification

Authors: Izad Behnia, Zhongshun Yuan, Paul Charpentier, Chunbao (Charles) Xu

Status: To be submitted to Int. J. Hydrogen Energy

Experimental work and data analysis were performed by Izad Behnia. Chunbao (Charles) Xu, Paul Charpentier, and Zhongshun Yuan provided consultation regarding experimental work and interpretation of results.

Chapter 4:

Supercritical water gasification of aqueous fraction of pyrolysis oil in the presence of a Ni-Ru catalyst

Authors: Izad Behnia, Zhongshun Yuan, Paul Charpentier, Chunbao (Charles) Xu

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Experimental work and data analysis were performed by Izad Behnia. Chunbao (Charles) Xu, Paul Charpentier, and Zhongshun Yuan provided consultation regarding experimental work and interpretation of results.

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Preface

“Well the basic thesis is that there's a god in heaven who is all powerful who wants to help people. And that - he will answer prayer, and does miraculous things in people's lives. And so I've documented some of these wonderful things” - Pat Robertson

To my Family

CHAPTER 1. INTRODUCTION

1.1. Energy from biomass

Bio-energy or energy obtained from biomass is widely considered to be a viable option for replacing fossil fuels. Depletion of fossil fuels and governments' ambition to reduce CO₂ emissions have motivated researchers to find a substitute which is clean, abundant, and carbon neutral. It is believed that 60% of the greenhouse effect comes from CO₂ emissions which are released through combustion of fossil fuels (UNFCCC, 2002). Since ancient biomass took millions of years to form, current fossil fuels are considered non-renewable (McKendry, 2002). Bio-energy is a renewable energy which comes from biomass. Biomass refers to any organic matter that is derived from plant based material. When this biomass is burned or thermo-chemically processed, chemical bonds between hydrogen, carbon, and oxygen molecules are broken. The solar energy which has been stored in C-C and C-H bonds through photosynthesis will be released in the form of energy. Since there is no net CO₂ production, this energy is considered green and carbon neutral.

Biomass may take various forms, but it is mainly composed of the following components, i.e. cellulose, hemicelluloses, lignin, proteins, lipids, and starches (Mohan et al., 2006). Water and inorganic compounds are also contained in biomass (Lu, H. and Baxter, 2011). Carbon and oxygen are the dominant elements in biomass which contribute almost 90 wt.% of the dry weight (Bolyos et al., 2003). Agricultural, forestry, and food processing residues are the major biomass resources. Agricultural biomass commonly has 15-17 GJ/ton heating values while this number is 18-19 GJ/ton for forestry biomass in comparison to 20-30 GJ/t for coal. Air-dried biomass usually consists of 15-20 wt.% moisture. Biomass bulk density is generally only 10-40% of that of coal. Biomass has extensively being used for energy in many countries, and it is currently the world's fourth largest energy source, contributing up to 14% of the world's primary energy demand (Veringa). Although renewable energy includes a relatively small portion of total energy supply, the installed renewable energy capacity has more than tripled between 2000 and 2009 (Merhej, 2012). Figure 1.1 shows the U.S. electric net generation from

2000-2009. It can be seen that biomass derived energy is gradually increasing from 1.9% in 2000 to 4.7% in 2009.

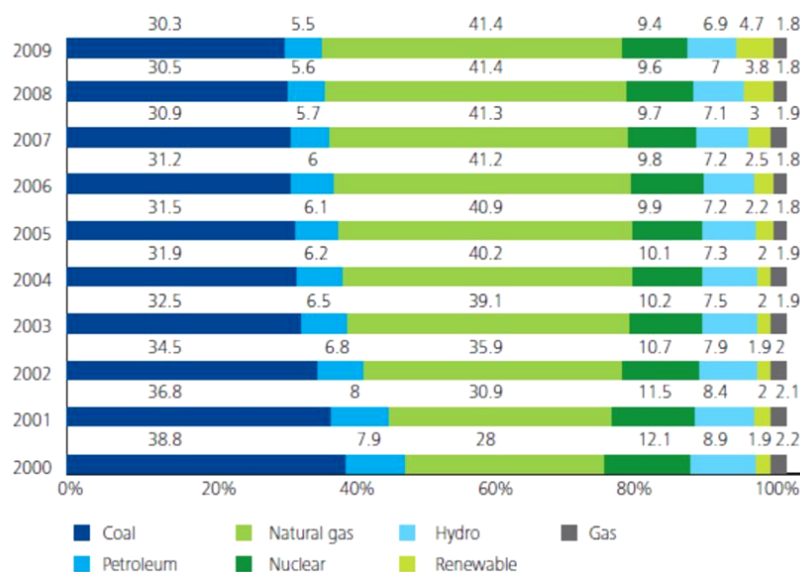


Figure 1.1 - U.S. electric net generation (2000-2009); reprinted (adapted) from (Merhej, 2012).

Biomass derived energy can be obtained from either thermo-chemical or bio-chemical processes (Ni et al., 2006). Thermo-chemical processes have received increasing attention since they are generally much faster and require a much less reaction time in comparison to days or weeks as required for bio-chemical or biological processes (Bridgwater, 2001). Moreover, a wider range of feedstock can be easily converted into energy with thermo-chemical processes compared to inefficiency with bio-conversion processes for some biomass feedstock (e.g., lignocellulosic materials) (Hemmes et al., 2003). Combustion, pyrolysis, gasification, and liquefaction are among the common thermo-chemical conversion processes, as compared in Figure 1.2. Depending on the selected thermo-chemical process, the products could be in form of heat, solid materials (e.g., charcoal), liquid fuels (e.g., bio-oils), and gases (e.g., fuel gases, syngas).

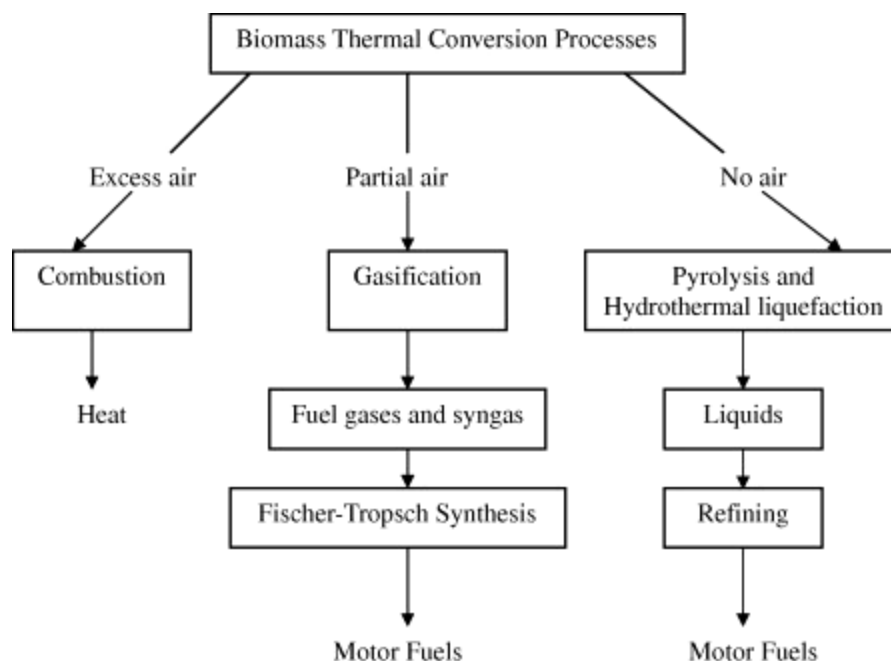


Figure 1.2 - Biomass thermo-chemical conversion processes; reprinted (adapted) with permission from (Demirbas, 2009). Copyright (2013), with permission from Elsevier.

Pyrolysis is currently the only large-scale technology for liquid bio-fuel production from biomass, and supercritical water gasification is a very promising technology for utilization of high water content biomass, although not yet commercialized. As such, the advantages and disadvantages of these two thermo-chemical processes- pyrolysis and gasification- are discussed in details as follows.

1.2. Pyrolysis

Pyrolysis refers to a thermo-chemical process in which thermal decomposition of feedstock takes place upon heating in the absence of oxygen. Depending on the residence time and temperature this process can be classified into three types: fast pyrolysis, intermediate pyrolysis, and slow pyrolysis. The final products obtained from pyrolysis are solid charcoal, liquid bio-oil, and gases. The pyrolysis liquid products (bio-oil) typically consist of complex mixture of oxygenated aliphatic and aromatic compounds as well as intermediate carbohydrates and other derivatives which have potential applications as liquid fuels and chemicals (Lehmann et al., 2011; Prakash and Karunanithi, 2009). Gas products can be utilized in the process via

burning to facilitate reactor heating while drying the incoming biomass feedstock (Balat et al., 2009). Depending on the type of pyrolysis, the products vary from solid to liquid to gas. Fast pyrolysis is operated under extremely short residence time (~ 1 s), at a temperature of 400-650 °C and a high heating rate (hundreds °C/min), which favors the formation of liquid products (Yanik et al., 2007). In contrast, slow pyrolysis has relatively longer residence time from hours to minutes and slow heating rates of 0.1-1 °C/s, while the operational temperature ranges from 400 – 600 °C. It can also yield approximately the same amounts of liquid, solid char and gas products (Demirbaş, 2001; Mohan et al., 2006).

Fast or flash pyrolysis, is so far the only technology demonstrated to be practical/commercially feasible on a large scale for the production of bio-oils from biomass. Fast pyrolysis offers an economically viable solution to convert bulky biomass feedstock into an energy intermediate product (bio-oil) with a significantly improved volumetric energy density. Bio-oil from fast pyrolysis however has high contents of oxygen (35-40 wt.%) and water (up to 50 wt.%), resulting in relatively low gross heating values (normally < 20 MJ/kg, only about half of that of petroleum). The high oxygen content is the major limitation for the utilization of bio-oil as liquid transportation fuel since it causes high viscosity, poor thermal and chemical stability, corrosiveness (acidity) and immiscibility with hydrocarbon fuels. As a result, bio-oil products require upgrading by reducing their oxygen content and increasing their H/C ratio before meaningful applications. Hydro-de-oxygenation (HDO) of bio-oils at 300-400 °C using conventional petroleum hydrotreating catalysts, i.e., CoMo and NiMo supported on γ -alumina, have been shown to be an effective technology for producing an oil product at 30-40 wt.% yield that contained a reduced oxygen content. These hydro-treated bio-oils with much improved heating values and hydrocarbon compatibility can be used as combustion fuels or may be mixed with petroleum feed for co-processing in existing refineries. However, the HDO process generates a high yield (up to 70 wt.%) of aqueous by-products (containing mainly water, as well as carbohydrate, phenolic compounds, acetic acids, and other organic compounds). This aqueous by-product stream contains a high TOC and must be treated before discharging to the environment.

1.3. Gasification

Gasification is a process in which carbonaceous materials such as biomass and coal are heated to high temperatures ($>700\text{ }^{\circ}\text{C}$) in the presence of oxygen or an oxidizer agent such as CO_2 or steam. The products are combustible gases such as H_2 , CH_4 , CO_2 , and CO . Gasification when employing oxygen or air is commonly referred to as partial combustion (Rezaiyan and Cheremisinoff, 2005). Gaseous products derived from biomass can be used for direct combustion for heat/power generation or for electricity generation with fuel cells. Compared with combustion, gasification process have advantages such as smaller footprints, higher thermal efficiency, and lower CO_2 emission (Beenackers and Maniatis, 1998). In a gasification process, biomass is heated to high temperatures which will form gas products through various chemical reactions. The product gas mixture mainly consists of H_2 and CO which are called syngas or synthesis gas. There are several chemical steps for the gasification process. First, biomass goes through pyrolysis reaction and decomposes into tar and volatile gases such as hydrogen, carbon monoxide, carbon dioxide, methane, hydrocarbon gas, and water vapor (E4tech, 2009). Part of the tar also cracks into smaller gas molecules at higher temperatures. The major reactions in biomass gasification include carbon gasification, water-gas shift and methanation reaction, as shown below.



Depending on temperature, pressure and substrate concentration, the gas products composition will vary. Generally, higher temperature and pressure favors more syngas (Haryanto et al., 2009). The required heat for gasification can be supplied by partial combustion of a portion of the biomass in the reactor (Juniper, 2007), or from external sources. Formation of tar during gasification may lead to lower gasification efficiencies, causing plugging of the reactor tubing, so it should be minimized as much as possible. The presence of a suitable catalyst and a well-designed gasifier can help tar reduction and hence enhance the gasification efficiency. The use

of catalysts makes it possible to operate gasification at lower temperatures, achieving similar efficiency as that of higher temperature (Abu El-Rub et al., 2004). Despite the advantages of gasification technology, there are also many challenges that may hamper application of this technology. For instance, successful gasification requires that the gasifier be designed for a particular type of feedstock (EAI catalyzing cleantech in India, 2013). Some types of gasifiers, e.g. updraft fixed bed, are very sensitive to the moisture content of the feedstock. Some gasifier require a long time to start up and produce a high tar-containing syngas that must be cleaned before it can be utilized for combustion in gas turbines or chemical synthesis (Rajvanshi, 1986).

1.3.1. Supercritical water gasification

Supercritical water gasification (SCWG) is a unique type of gasification technology that is capable for gasifying high water content biomass. Supercritical water is water above its critical points (374 °C and 22.1 MPa). At supercritical conditions, there is no distinctive boundary between the liquid and gas phases. Water at these conditions shows high solubility of organic compounds due to weekend hydrogen bonding. Figure 1.3 shows the characteristics of water at 3400 psig vs. temperature.

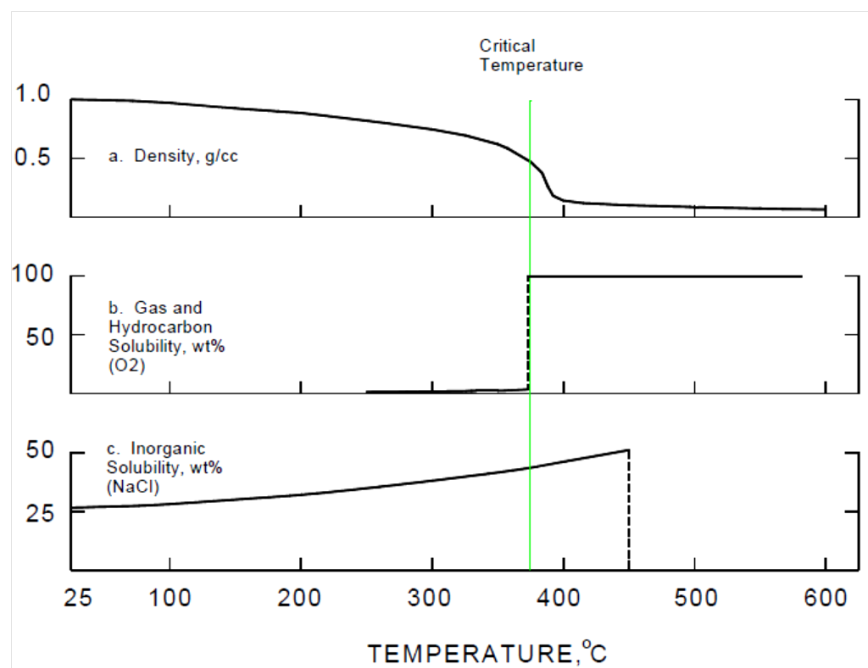


Figure 1.3 - Characteristics of water at 3400 psi as a function of temperature. a. Density. b. Solubility of non-polar organics and permanent gases. c. Solubility of sodium chloride. (Hong and Spritzer, 2002)

Due to the high reactivity and solubility of supercritical water for organic compounds, it is an ideal gasification medium. Comparing SCWG with the traditional gasification methods, a lower amount of tar was observed in biomass SCWG (Xu and Antal 1998). SCWG has shown its promise for hydrogen production from biomass at high temperatures ($>700\text{ }^{\circ}\text{C}$) (Florin and Harris, 2007) and methane production at lower temperatures ($<600\text{ }^{\circ}\text{C}$) (Elliott et. al., 1998, 1990).

Although SCWG technology is still a relatively new method for biomass gasification, a wide range of biomass feedstocks have been studied. Model compounds such as glucose (Zhang et. al., 2011) and lignin (Sato et al., 2005) were used in SCWG, helping to investigate the mechanism of SCWG. However, there are many challenges for gasification of real biomass feedstocks such as sawdust (Yoshida et al., 2004) and sewage sludge (Chen et. al., 2013). As discussed previously, the aqueous by-product stream from HDO of bio-oils or the aqueous fraction of bio-oil needs to be treated to reduce its TOC and to recover energy. SCWG can be a promising technology for treatment of such high water-containing waste streams. Conversion of

such waste stream into hydrogen and methane fuel gases would yield both economic and environmental benefits. Whereas, to the best of the author's knowledge, SCWG of these feedstocks have not yet been studied. Thus, the present study targets to convert aqueous fraction of fast pyrolysis oil into methane and hydrogen gases via SCWG, where development of highly active catalysts is the research focus in this study.

1.4. Overview of this thesis

Chapter 1 provides a brief introduction to various thermo-chemical technologies for conversion of biomass into bioenergy. The advantages of two types of thermo-chemical processes, i.e., pyrolysis and gasification (in particular, SCWG), were introduced in details in this chapter.

A literature review on SCWG is provided in chapter 2. Different operational parameters that affect SCWG are discussed in this chapter, focusing on effects of temperature and catalyst design. Engineering concepts for generating either hydrogen or methane rich gas were also presented in this chapter.

Chapter 3 investigates the SCWG of glucose-water solution as a model compound at a relatively low temperature. Catalysts with different nickel and ruthenium loading on various supports were studied to screen out the best catalyst (with higher activity and stability) for SCWG of biomass.

In chapter 4, using the best catalyst obtained from Chapter 3 studies, effects of temperature and substrate concentration on SCWG of glucose were examined. Moreover, SCWG of aqueous fraction of pyrolysis oil was also studied in the presence of the best catalyst from chapter 3.

Chapter 5 presents overall conclusions from the thesis research and recommendations for future studies.

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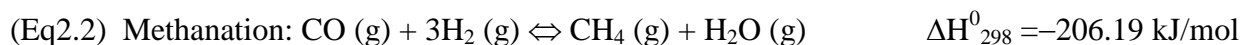
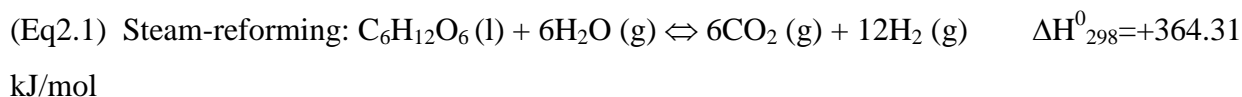
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CHAPTER 2. LITERATURE REVIEW

2.1. Supercritical water gasification (SCWG)

Supercritical water (SCW) is water above its critical point (374 °C, 22.1 MPa), which has properties different from those of steam or liquid water. In particular, the low polarity of SCW makes it an ideal solvent for non-polar compounds and gases, which eliminates the mass transfer limitation between different phases in a reaction system. SCW can be employed as a suitable solvent or reactant for reactions, e.g., supercritical water gasification (SCWG) of biomass for renewable hydrogen generation. SCWG can enable shorter residence times and smaller reactor volumes or a smaller footprint for the process. In the SCWG of biomass, many possible reaction pathways are possible. Using glucose as the model biomass compound, the major gas products that have been identified are: H₂, CO₂ as well as CO and CH₄, depending on reaction conditions (Matsumura et al., 2005; Zhang et al., 2011a):



At relatively lower temperatures (in the vicinity of the critical point) and with the presence of a suitable catalyst, the gasification reactions lead to significant formation of methane-rich gas products, while at higher temperatures, H₂ is the dominant gas product (Matsumura et al., 2005).

The water-gas shift reaction is a weak exothermic reaction ($\Delta\text{H}_{298}^0 = -41.16 \text{ kJ/mol}$) compared with the methanation reaction ($\Delta\text{H}_{298}^0 = -206.19 \text{ kJ/mol}$), so it is more thermodynamically and kinetically favorable at temperatures far above water's critical temperature. However, low temperatures favor the methanation reaction, leading to methane-rich gas (Elliott and Sealock, 1985; Osada et al., 2003). An equilibrium model calculation shows that maximum CH₄ production is achievable when the gasification reaction operates at a lower temperature but at

higher pressure (Mozaffarian et al., 2004; Voll et al., 2009), while pressure does not have a significant effect on the gas distribution at high temperatures ($>550\text{ }^{\circ}\text{C}$) (Antal et al., 1993). Substrate concentration also plays an important role in the gas product composition. It has been shown (Yu et al., 1993) that the total carbon efficiency and H_2 yield dropped when increasing the substrate concentration, whereas the CH_4 and CO_2 yields increased. Although higher concentrations of organic feedstock are more favorable for CH_4 production, this results in simultaneously higher tar and char yields. Therefore, suitable catalysts are critical in the process to speed up the steam-reforming reactions of tar/char while reducing the yields of tar and char.

2.1.1. Methane and hydrogen production

Since fossil fuels will become increasingly expensive and hard to obtain in the future, it is essential to find a reliable and economical renewable energy source. Due to the many advantages of hydrogen as a fuel, many groups have tried to find a hydrogen resource. Although hydrogen is an abundant element, it does not occur naturally and is normally bonded with organic compounds. Some innovative technologies have been suggested to split hydrogen from hydrocarbons into pure hydrogen gas. Electrolysis of water has been a traditional way to produce this energy carrier gas (Turner, 2004). Photolytic processes are another viable option if the efficiency of this technology can be improved to support the economic costs. Traditional gasification processes are also another possible way, but they are limited to only low water content feedstocks (Elliott, 2008). Nevertheless, SCWG is a promising method to produce hydrogen gas with a high efficiency and at a high pressure-suitable for storage. This hydrogen can be used in the anode side of fuel cells, which produce only water as the end-product (Zhang, 2008).

Depletion of fossil fuels and environmental issues concerned with burning of these fuels such as CO_2 emission and global warming have intensified the efforts worldwide to secure alternative sources of energy. Methane is considered to be more eco-friendly fossil fuel than other hydrocarbon fossil fuels (coals and petroleum), as it generates less CO_2 emission per joule of heat. Methane has 802.6 kJ/mol net enthalpy of combustion, and the ratio of heat of combustion to the molecular mass demonstrates that methane as the simplest hydrocarbon releases more heat per mass unit (50.2 kJ/g) than other complex hydrocarbons (green and Perry, 2008). Methane can be used as a fuel in turbines, steam boilers, heat for households, or in car engines.

Natural gas with 95% methane content is a rich source of methane. This natural gas is piped for domestic heating and cooking purposes throughout the world. In a recent speech by the US president Obama on June 25, 2013 at Georgetown University in Washington DC, it was reaffirmed that the US government will commit burning “cleaner natural gas instead of dirtier fuel sources (e.g., coal) for power generation ("The Realities of Climate Change, presidential rhetoric by president Barack Obama," 2013). As is well known, a common route to generate methane-rich bio-gas is anaerobic digestion, but biological processes face many challenges such as a large footprint (large reactor and land requirement), low reaction rates (days to weeks reaction) and low tolerance of bacteria to different types of feedstock (Matsumura, 2002).

Among all the hydrothermal processes, SCWG has several advantages which make it a unique media to convert organic biomass into either methane or hydrogen gas. Temperature plays a key role in this process which will be discussed in Section 2.2.1. In a general look at SCWG, higher temperatures generate more hydrogen, and by decreasing the temperature the gas distribution shifts towards more methane production (Matsumura et al., 2005; Mozaffarian et al., 2004).

Eq2.4 shows that the methanation reaction is a highly exothermic reaction which means it requires less external heat to maintain the desired reaction temperature than the water-gas shift reaction. Additionally, operation at low temperatures can improve the cold gas efficiency of the process and utilize waste heat from other high-temperature processes (i.e. iron/steel manufacturing) (Lee et al., 1999, 2002). However, for CH₄ production via low-temperature SCWG of biomass, the presence of an active catalyst is critically important for reducing the tar/char yields and increasing the carbon conversion rate. Experimental results without employing any catalyst by Lee et. al. (2002) from SCWG of glucose solution depicts that at 700 °C complete carbon gasification is achieved and no tar or char remains in the system.

Early studies on biomass SCWG proved that methane-rich gas can be achieved at lower temperatures (<500 °C), whereas high yields of hydrogen are plausible at above 600 °C (Guo et al., 2010; Yanik et al., 2008; Zhang et al., 2011a). To increase hydrogen generation, the water-gas shift reaction should proceed close to the thermodynamic equilibrium, and the methanation reaction should be diminished by lowering the reactor residence time and increasing

temperature (Byrd et al., 2007). Zhang et al. (2011a) studied gasification of a 5 wt.% aqueous glucose solution at 600 °C showing production of hydrogen-rich gas, 38.4 mol/kg glucose, with a low concentration of methane, where it was also found that reduced nickel catalyst favored the water-gas shift reaction, and ruthenium suppressed tar and char production. 0.22 (gr CH₄)/(gr of wood) was achieved at 450 °C and 34 MPa from wood flour using a nickel catalyst (Sealock et al., 1988). SCWG of lignin and cellulose in the presence of Ru/TiO₂ at 400° C in a bath reactor led to 31% and 74% carbon conversion, respectively, and gas products consisting of CH₄ as the main component (41~45 vol%) (Osada et al., 2003). Park and Tomiyasu (2003) almost completely gasified cellulose at 450 °C for 120 min in a batch reactor using RuO₂ catalyst, producing a gas product containing CH₄ (34 vol%), H₂ (14.6 vol%) and CO₂ (50.9 vol%). Elliot et al. (2004) achieved complete gasification of dairy manure at 350 °C over a Ru/C catalyst, generating a produced gas comprising almost 50 vol% CH₄. Hydrogen was dominantly produced from sugars and alcohols at temperatures near 227 °C in a single-reactor aqueous-phase reforming (APR) process using a platinum-based catalyst (Cortright et al., 2002). It was also found that the selectivity for hydrogen production increased more when reduced molecules were used compared to sugars, e.g. using ethylene glycol and methanol gave almost completely hydrogen and carbon dioxide conversion at a small weight hourly space velocity (WHSV) was achieved. The results from APR of biomass suggest that the catalyst plays a critically important role in the gasification of biomass in subcritical/supercritical water. (Cortright et al., 2002)

2.1.2. Thermodynamics of SCWG process

As shown in Figure 2.1, thermodynamic equilibrium calculation of SCWG of biomass (using Lactide, C₆H₈O₄ as a model compound) reveals that H₂ is the main gas product at high temperatures, but temperature does not influence the CO₂ concentration significantly. In contrast, at low temperature, CH₄ dominates in the gas products although lower temperatures favor tar/char formation and reduced gasification efficiency (Elliott, 2008; Kee et al., 2001).

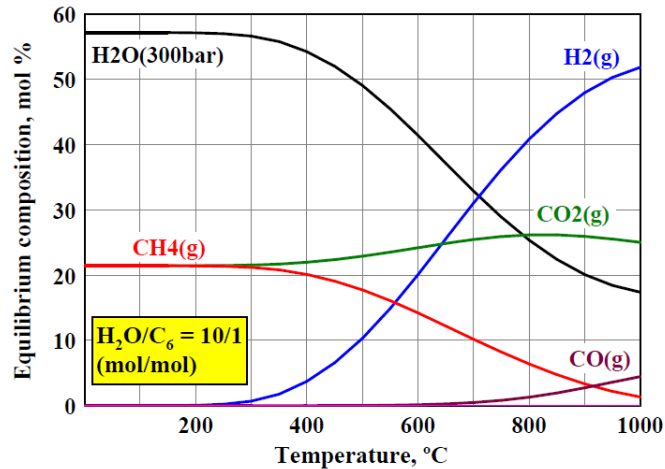


Figure 2.1 - Equilibrium gas composition of biomass model compound (Lactide, $C_6H_8O_4$) under subcritical and supercritical water ($C_6/H_2O = 1/10$ mol/mol) at 30 MPa (Ohtsuka, 2012)

SCWG operation can be classified into three regions based on the operating temperatures, i.e., sub-critical, low temperature supercritical and high temperature supercritical operation (Osada et al., 2006).

Region I (500-800 °C) - the high temperature supercritical region: Gasification reactions of biomass are greatly promoted in this region, but a catalyst is still desirable to enhance the hydrogen yield and carbon conversion while avoiding char formation. In this region, catalysts such as alkali compounds promote the water-gas shift reaction towards production of hydrogen-rich gas. Zhang et. al. (2011b) utilized novel $RuNi_{10\%}/\gamma-Al_2O_3$ catalyst for gasification of glucose, simulated aqueous biomass (glucose, acetic acid, guaiacol) and an aqueous waste stream from wastewater sludge hydrothermal liquefaction process. For all these biomass feedstocks, approx. 100% carbon conversion was achieved into gaseous products, mainly H_2 at >650 °C.

Region II (374-500 °C) - the low temperature supercritical region: A catalyst is required to facilitate hydrolytic degradation of biomass and the subsequent reforming/gasification reactions. A high yield of tarry materials is expected in this region due to the favorable conditions for re-polymerization of the hydrolytic products. The presence of suitable catalysts

such as noble metal catalysts can effectively reduce tar formation and promote the gasification reactions (Calzavara et al., 2005).

Region III (below 374 °C) - subcritical region: in this region, biomass feedstock is more likely to be liquefied to obtain bio-crude oil products via hydrothermal liquefaction/gasification, while aqueous phase reforming (APR) of biomass is possible but the process is slow as expected and requires some noble metal catalysts (Matsumura et al., 2005).

The chemistry involved in a hydrothermal gasification is relatively complex, which makes it difficult to uncover the mechanism of methane formation under the harsh SCWG conditions. Elliott and Sealock (1996) suggested the overall stoichiometric reaction for gasification of cellulose as a carbon source feedstock at 350 °C and 21 MPa is as follow: $C_6H_{12}O_6 (l) + H_2O (g) \rightarrow 3CH_4 (g) + 3 CO_2 (g)$. Some possible reaction pathways were proposed to describe the catalytic reactions of biomass (phenol) gasification in SCW using Ni/C catalyst (Sharma et al., 2006), which will be discussed in the following sections.

In this literature review, we focus on Region II and how other operating conditions can affect SCWG in this temperature range. This is due to the focus on methane production, as methane is thermodynamically favored in this temperature zone. .

2.2. Effects of operating conditions on SCWG of organics

2.2.1. Temperature

Although, operation at lower temperatures is economically favored comparing to higher temperatures in terms of the operating costs, higher temperatures facilitate better biomass conversion and product yields. It is still a major challenge for the operation of a flow-type reactor at low temperatures due to the formation of tar and char, which cause reactor plugging. On the other hand, severe operational conditions with high temperature supercritical water also poses great challenges on equipment, requiring special alloys for reactor construction due to the higher operating pressure and increased corrosion problems for high temperature SCWG processes.

As discussed previously in this chapter, there are many studies on hydrothermal conversion of wet biomass either at high or low temperatures. SCWG of 1 wt.% glucose in a capillary reactor shows that increasing reaction temperature raises gas production for both methane and hydrogen. This effect is more intense for hydrogen, but methane gas is still slightly increased. For instance, from 500 to 800 °C, the hydrogen yield increases from almost 1 to 5.5 mol/mole of glucose, while this number goes from 0 to 0.75 mol/mol for methane using glucose (Kersten et al., 2006). At 360 °C and 3000 psig pressure, high methane production from four different feedstocks, P-Cresol 2%, cheese whey, lactose 10%, and lactose 5 wt% in a continuous-flow tubular reactor over different commercial Ni catalysts was observed (Elliott et al., 1990). It was also demonstrated that 94.3, 94.3, 87.5, and 94.8% carbon was converted into gas products, high in CH₄. In another research, aquatic and food waste materials with 1-20 wt.% carbon composition were treated using near-/supercritical water at 350-450 °C to obtain methane-rich gaseous products (Elliott et al., 1988). Experiments by different research groups on low-temperature supercritical water gasification proved that high methane gas production occurs under condition, which supports the thermodynamic predictions. However, the lower temperature leads to more tar and char formation in non-catalytic SCWG. To overcome these un-desirable side products, different catalysts are commonly examined.

2.2.2. Types of catalysts

Metallic catalysts (Ni, Ru, etc.) are commonly used for production of methane with SCWG of biomass. However, the major challenge for using metallic catalysts for SCWG reactions is that the harsh condition of SCWG which causes oxidation of the catalyst. Both the catalyst and support should remain stable in the hot compressed water environment. An efficient catalyst is one with stability and high activity during the long reaction time, good selectivity towards the desirable products, high carbon gasification efficiency, and reasonable cost. Common problems responsible for deterioration of catalyst stability and activity in SCWG are sintering, phase transformation, and changes in the surface properties. Catalytic hydrothermal gasification of biomass model compounds, glucose, cellulose, fructose, xylan, pulp, lignin and bark have been studied in the presence of Ni/ α -Al₂O₃, Ni/hydrotalcite, Raney nickel, Ru/C, and Ru/ α -Al₂O₃ catalysts at 350 °C in a batch reactor (Azadi et al., 2012). It was observed that with nickel and ruthenium based catalysts high methane production was achievable. Among a variety of

catalysts studied, Ni and Ru are believed the most efficient catalysts under SCW conditions. These are also effective catalysts for reducing tar and char formation in low temperature SCWG (Osada et al., 2006). Ruthenium has also been used as a co-catalyst to promote the performance of Ni catalyst by decreasing char formation (Zhang et al., 2011a). A high active and stable, even after 200 hours of operation, Ni/Carbon catalyst was utilized for treating wastewater samples from a coal dewatering process, and no sintering was observed (Sharma et al., 2006). Another study in presence of a novel Ni-Ru catalyst demonstrated high activity and stability of this catalyst over 33 hours for gasification of 5 wt.% glucose-water solution at 700 °C and 24 MPa (Zhang et al., 2011a). Among all the investigated catalyst support materials, carbon, zirconium and alumina are believed to be the most stable supports in the SCW environment (Elliott, 2008; Lee and Ihm, 2008; Elliott et al., 1993a). However, a significant loss of carbon catalyst activity during SCWG operation has been reported (Xu et al., 1996). For example, many metallic catalysts supported on coconut shell activated carbon lost activity after 4 hour on stream in SCWG of glucose at 600 °C. Nickel and copper catalysts showed superb stability in the process. However, copper is not normally as active as ruthenium or nickel (Elliott, 2008). Summary of wide range of catalysts based on their stability and activity in hot compressed water environment at 350 °C is presented in Table 2.1 (Elliott and Sealock, 1996).

Table 2.1 - Summary of different catalysts and supports used in SCWG (Elliott and Sealock, 1996).

Useful Catalytic Metals	Inactive Metals	Metals Oxidized at Conditions	Stable Supports	Unstable Supports	Hydrolyzable Supports
Ru	Pt	Co	α -Al ₂ O ₃	MnO ₂	γ -Al ₂ O ₃
Rh	Pd	Fe	ZrO ₂	SiO ₂	δ -Al ₂ O ₃
Ni	Cu	Cr	C	Ca/aluminate	η - Al ₂ O ₃
	Ag	Mo	TiO ₂	Kieselguhr	SiO ₂ / Al ₂ O ₃
	Rc	W			
	Pb	Zn			

As shown in Table 2.1, noble metal catalysts, Ru and Rh, are very stable with satisfactory lifetime under hydrothermal gasification conditions, and have been widely used in SCWG process (Elliott and Sealock, 1988; Elliott, 1993b; Kersten, 2006; Osada et al., 2006). However, a considerable limitation of these noble metals is their high price.

2.2.2.1. Nickel catalysts

In a study by Sealock et al. (1988), nickel catalysts were applied for SCWG of various high moisture-containing biomasses, and the results are summarized in Table 2.2. The nickel catalyst shows great potential for catalyzing methanation reaction at 400 °C leading to very high carbon conversions. However, the catalyst in this study exhibited poor stability. It was also observed that addition of alkali to the catalytic system led to an increase in hydrogen production accompanied by a reduced methane yield.

Table 2.2 - Low-temperature gasification of high-moisture biomass feedstocks with Ni-catalyst at 400 °C (Elliott et al., 1988).

Feedstock	Carbon gasification efficiency, %	CH ₄ scf/lb	H ₂	CH ₄	CO ₂	CO	C ₂
Cellulose	97.6	5.5	3.9	43.2	47.8	0	3.7
Sorghum	94.6	5.5	9.5	38.4	50.5	0	1.6
Sunflower	87.8	5.1	5.0	45.7	45.5	0	2.4
Napler grass	100.8	5.2	6.9	40.6	51.1	0	1.4
Corn stover	72.9	1.5	20.1	16.3	62.0	0	1.3
Water hyacinth	73.1	4.0	11.3	35.9	49.6	0.8	0.9
Kelp	78.8	2.9	7.1	41.9	48.4	0	1.5
Douglas fir	49.8	2.6	21.6	29.0	47.6	0	1.8
Grape pomace	44.5	3.1	9.6	40.2	47.7	0	1.0
Spent Grain	55.7	3.9	9.6	43.1	44.2	0	1.4
Potato waste	46.4	2.0	27.6	20.4	50.2	0	1.8

Lee and Ihm (2008) demonstrated high stability and activity of 16 wt.% Ni/AC catalyst for the gasification of concentrated 0.6 M glucose at 575-725 °C in a packed bed reactor. Based on a patent by Elliott and Sealock (1988), there was a direct relation between methane formation and concentration of the reduced nickel catalyst: in low-temperature SCWG, more nickel would result in higher methane formation. Sato et al. (2005) observed that increasing nickel loading on a MgO support produced more methane in the SCWG of lignin. Again, as a common observation in many studies, increase nickel metal loading promotes gasification efficiency and increases yields of various gas products, in particular methane formation. This metal is also able to catalyze the water-gas shift reaction in the high temperature SCWG zone. Thanks to Ni/ γ -

Al₂O₃ (10 wt.% Ni, 90 wt.% alumina), Zhang et al. (2011a) were able to achieve H₂ yield of 38.4 mol/kg glucose at 600 °C in a flow reactor.

Some possible reaction pathways were proposed as follows to describe the catalytic reactions of biomass (phenol) gasification in SCW in the presence of a Ni catalyst supported on carbon (Ni/C) by Sharma et al. (Sharma et al., 2006):

- I. Decomposition of large molecules into smaller molecules at an elevated temperature;
- II. Steam gasification of the small molecules into CO and H₂ (steam reforming reaction);
- III. Methanation and water-gas shift reaction of CO to produce CH₄ and CO₂ over metallic catalysts

Reduction of water by Ni: $\text{Ni} + \text{H}_2\text{O} \rightarrow \text{NiO} + \text{H}_2$ (step 1)

Reduction of organic compounds by Ni:

$\text{C}_6\text{H}_5\text{OH} + n \text{Ni} \rightarrow \text{C}_6\text{H}_x \text{Ni}_n + (2-x) \text{H}_2 + \text{H}_2\text{O}$ (step 2)

Reduction of NiO: $\text{C}_6\text{H}_x \text{Ni}_n + 6\text{NiO} \rightarrow 6\text{CO} + (x/2) \text{H}_2 + (6+n) \text{Ni}$ (step 3)

Methanation reaction: $3\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O}$ (step 4)

Water-gas shift reaction: $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2$ (step 5)

The non-stoichiometric overall reaction: $\text{C}_6\text{H}_5\text{OH} + \text{H}_2\text{O} \rightarrow \text{CH}_4, \text{C}_2\text{H}_6, \text{H}_2, \text{CO}_2$

As expected, nickel is oxidized by water to form nickel oxide (step 1). Ni metal can also reduce organic compounds to form organic Ni compounds as a reducing agent (step 2). This would reduce NiO back to Ni metal (step 3). Meanwhile, methanation and water-gas shift reactions take place in the reactor systems. Overall, formation of CO, H₂, CO₂, and CH₄ over Ni catalyst surface can be realized.

2.2.2.2. Ruthenium catalyst

As introduced briefly previously, Ru is also a highly active metallic catalyst or co-catalyst for SCWG of aqueous biomass (Elliott and Sealock, 1988; Elliott et al., 1993a; Baker et. al., 1997; Kersten et al., 2006; Lee and Ihm, 2008). Results of gasification of p-cresol at 350 °C and 20 MPa over different ruthenium catalysts in a batch reactor are summarized in the Table 2.3. As it is clearly shown in this table, Ru showed a higher activity than the other noble metal catalysts (Rh, Pt, Pd) for SCWG.

Table 2.3 - Performance of different Ruthenium catalysts in SCWG of p-cresol at 350 °C and 20 MPa (Lee and Ihm, 2008)

Catalyst	carbon gasification efficiency, %	Gas composition, vol%			Time (min)
		CH ₄	CO ₂	H ₂	
5% Ru/ γ -Al ₂ O ₃	89.1	58.9	38.8	1.0	90
5% Ru/ δ -Al ₂ O ₃	43.5	55.2	35.9	7.7	120
5% Ru/ZrO ₂ (reduced)	28.5	49.0	35.6	13.4	90
3% Ru/ γ -Al ₂ O ₃	18.8	40.9	37.3	20.6	120
5% Ru/carbon	21.4	24.1	58.6	10.2	110
1% Ru/carbon (reduced)	17.3	40.4	42.3	8.4	125
5% Ru/ α -Al ₂ O ₃ (reduced)	0.01	0.5	0.6	98.5	120
5% Ru/carbon (reduced)	26.6	57.5	36.3	2.3	125
1% Rh/ γ -Al ₂ O ₃ (reduced)	7.06	42.1	39.1	14.4	110
1% Rh/ α -Al ₂ O ₃	1.54	12.7	32.9	52.5	105
5% Pt/ γ -Al ₂ O ₃	1.29	26.9	63.1	3.9	90
5% Pd/ γ -Al ₂ O ₃	0.42	11.0	29.3	59.8	95
2% Pd/carbon (reduced)	1.20	7.2	56.3	35.2	90

It is reported that addition of ruthenium as a co-catalyst to nickel catalyst could retard sintering and crystallization of nickel particles, which might account for its positive effect on enhancing carbon conversion in the SCWG of biomass (Elliott and Sealock, 1988). However the effect on gas distribution was found to be minimal. At high temperatures and low substrate concentrations, Ru proved to be a very active catalyst for improving hydrogen generation and reducing methane formation in SCWG (Byrd et al., 2007a). Thus, ruthenium can both help reduce and increase methane formation in SCWG of biomass, depending on the operational conditions. It was also reported that ruthenium suppressed the methanation reaction at 700 °C and 248 bar for SCWG of 1 wt.% glucose.

2.2.3. Pressure

The total pressure of the reaction system does not appear to have a significant effect on SCWG of biomass. The pressure effect on SCWG of glucose was studied at 600 °C to find the relation of this parameter with gas distribution (Xu et al., 1996). Although, higher pressures did not significantly affect carbon conversion, pressure slightly influenced gas distribution. Equilibrium data for SCWG of pyrocatechol (Kruse et al., 2000), depicted that pressure can change gas products at very high temperatures, > 700 °C, and this influence was stronger for producing hydrogen gas. It is, however, not economically wise to increase the reactor pressure due to the increased capital costs required for both compression and equipment needed at higher pressures.

2.2.4. Substrate concentration

Apart from temperature, catalysts and pressure, the substrate concentration is another important factor affecting gasification efficiency. Kinetically, a higher substrate concentration enhances the reaction rate, but it would lead to reduced conversion base on the thermodynamic equilibrium equations. This is due to the reduced water fraction in the reactor system. The SCWG of glucose over ruthenium catalyst at 600 °C and 300 bar was shown to decrease the yields of H₂ and CO₂ with increased substrate concentration. However, the CH₄ yield also increases with increasing substrate concentration. In another words, higher yields of H₂ and CO₂ are generally favored at a lower substrate concentration. This can be easily explained as

high water content drives the equilibrium of the steam-reforming reaction toward H_2 and CO_2 production (Elliott, 2008).

Thermodynamic equilibrium calculations help predict the increase of methane production at a higher substrate concentration and a lower temperature (Mozaffarian et al., 2004). However, high concentration of carbon in the substrate may lead to char and tar agglomeration and further reactor plugging. A study of substrate concentration on gasification of glucose demonstrated that higher substrate concentration significantly decrease gas yields, and this effect hydrogen production the most (Kersten et al., 2006).

2.2.5. Alkali salt effects

Alkali salts can catalyze the water-gas shift reaction. In a study by Gadhe and Gupta (2005), it was shown that the H_2 yield increased considerably with the addition of K_2CO_3 . Reducing the methanation reactions also will happen by adding K_2CO_3 or KOH to the aqueous methanol feed. Alkali salts in the feed stream can cause hydrogen production increase and CO production decrease through shifting the water-gas shift equilibrium to product formation (Hao et al., 2003; Kruse et al., 2010; Matsumura et al., 2005). Salts including KOH , $KHCO_3$ and K_2CO_3 have a significant influences on the conversion of model substances such as glucose and pyrocatechol (Kruse et al., 2000). Among the alkali salts, Na_2CO_3 helps increasing gasification efficiency to achieve 100% carbon gasification efficiency in a short resident time (Hao et al., 2003). However, because of the lower solubility of salts in SCW compared to liquid water, plugging may happen due to salt precipitation.

2.3. Tar and char

Unconverted biomass can form char, while tar comes from undesired reaction products (Calzavara et al., 2005). Formation of tar and char in a biomass SCWG process will result in a considerable loss of gasification efficiency (Mozaffarian et al., 2004). The formation of tar/char is intensified at a lower temperature or a higher feed substrate concentration or at a low heating rate (Matsumura et al., 2005; Xu et al., 1996). Formation of char and tar during gasification limits the efficient production of methane and hydrogen and biomass conversion. Tar formation is more favored at low temperatures and longer residence time (Xu et al., 1996) while at a higher temperature above 700 °C, most of tars can convert into gas (Matsumura et al., 2005). A

successful conversion of tarry materials into gas is achievable by increasing temperature up to 700 °C, whereas char remains unconverted. This may lead to deposition of char/coke over catalysts' surface with a later loss of the catalyst's activity (Delgado et al., 1997). Hydrothermal gasification of cellulose at 200-350 °C in a batch reactor proved that alkali compounds such as Na_2CO_3 could inhibit tar and char formation (Minowa et al., 1998). The presence of alkali compounds also reduced the degradation temperature of cellulose, and promotes hydrogen production.

On the other hand, in the presence of an alkali catalyst, char formation might be very low in the reactor, but it can still causes problems including plugging due to the formation of coke, at low temperatures. When the biomass water mixture is heated for a long time at subcritical temperatures, furfurals and other unsaturated compounds are formed that may polymerize from the formation of free radicals above the critical temperature (Matsumura et al., 2005). The main by-products in SCWG of glucose are fructose, dihydroxyacetone, glyceraldehydes, erythrose, glycolaldehyde, pyruvaldehyde, 1,6 anhydroglucose, acetic and formic acid, and 5-HMF (Kabyemela et al., 1999). Then, through repolymerization of these ring compounds, solid char/coke particles form. It is also believed that 5-HMF is the key intermediate that causes repolymerization reaction resulting in coke formation (Chuntanapum and Matsumura, 2010) via the pathway, illustrated in Figure 2.2.

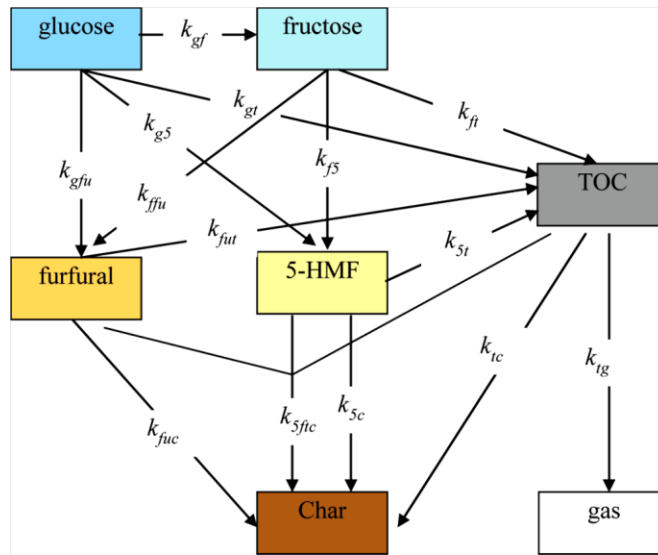


Figure 2.2 - Proposed formation pathways for char/coke in SCWG of glucose reprinted (adapted) with permission from (Chuntanapum and Matsumura, 2010). Copyright (2013) American Chemical Society

2.4. Reactor

One of main challenges for hydrothermal gasification is to choose appropriate reactor wall materials due to the severe operating condition of SCW causing material corrosion. Any small cracks caused by corrosion may rupture the wall or junctions. There are several possible reasons for material corrosion in the reactor, including:

- I) Chemical corrosion: acidic components, produced as intermediate components and dissolved CO_2 in hot water may cause corrosion.
- II) Hydrogen embrittlement: generated by high partial pressure of hydrogen gas.
- III) Stress corrosion cracking: chloride or alkali is considered as another reason of corrosion (Elliott and Sealock, 1996).

SCWG conditions can cause extremely severe metal corrosion problem through etching the oxidized coating layer on steel walls. In low temperature gasification, hydrogen embrittlement, is not a serious concern because of the low partial pressure of hydrogen. Although in reality, working with biomass may contain alkali and chloride, which can causes corrosion too.

Table 2.4 - Summary of stressed coupon test for investigation of material's corrosion (Elliott and Sealock, 1996).

1020 mild steel, 2.5 Cr/1Mo steel,	Abrasion of formed black oxide might increase corrosion in a non-static environment loading
374stainless steel, 316L stainless steel, 304L stainless steel	316L stainless steel based on its corrosion ($0.1\mu m$) vs. cost is the most useful material
Inconel 600, Inconel 625	High resistance to corrosion, but high cost of materials limits their applications

Titanium is well known to have a superb resistance to corrosion, but it has low pressure resistance. High pressure environments also cause mechanical damage, which limits the reactor design. Thus, it is not appropriate to build a reactor totally from titanium.

Different alloys contains various metals such a nickel and carbon which may participate in the various catalytic reactions. To avoid these side effects, scientists usually run a blank experiment (without catalyst) for at least 100 hours to prevent the wall catalytic effect (Guo et al., 2010; Zhang et al., 2011b).

SCWG of biomass is a new process which is still under development. Different research groups have utilized various different types of reactors such as capillary, batch, and continuous reactors. Batch autoclaves are suitable reactors to examine the gas production yield and carbon conversion into hydrogen or methane. Quartz capillaries as batch micro-reactors are very efficient in terms of being able to run at high speeds and are relatively inexpensive tests. Additionally, various visual techniques can be used to record events occurring inside the capillary (Mozaffarian et al., 2004). Continuous reactors are more interesting since they can be scaled up for production of syngas or SNG in large scale. However, these reactors are challenging to operate as plugging may occur.

There are also many challenges hindering the commercialization of SCWG technologies. One common difficulty is feeding viscous solid feedstocks into a high pressure environment. The nature of biomass feedstock varies from dilute waste streams to heavy slurries of biomass in

water. The original biomass, coarse or fibrous such as municipal waste, would need to be ground and mixed with water to enable pumping. For highly viscous streams, high pressure pumps can be applied as a possible solution, which would however increase the capital costs.

Although many small reactors have been used in laboratories (e.g., University of Hawaii, Osaka Gas, Pacific Northwest National Laboratory, FzK, Hiroshima University, and in the University of Twente, and BTG company), large scale industrial plants do not yet exist. However, Forschungszentrum Karlsruhe (FzK) in Germany is the largest plant working on SCWG. This large scale reactor with about 100 L/hour capacity was built to investigate the commercial gasification of wet residues from wine production. This pilot plant called VERENA is for gasifying agricultural materials with maximum 20 wt.% solid content under working pressure up to 35 MPa. VERENA is the first completed continuous operating plant worldwide for SCWG. Employing VERENA, SCWG of corn silage produces a gas product consisting of 36 vol% methane and 45 vol% hydrogen.

The first generation of pilot plant for supercritical water gasification with a capacity of 30 L/hour was developed at the University of Twente, Netherlands (Nanou, 2013). Several studies with non-fouling feedstocks were performed and no plugging was observed. The results were also compatible with continuous reactors and microreactors. Glycerol and methanol were successfully gasified at 650 °C and under about 300 bar. Experiments with more complex feedstocks had some operational problems such as fouling and heat-exchanger's blockage. In their design, they used a double-walled heat exchanger between the inlet and outlet streams to achieve a reasonable efficiency. By flowing the feedstock through the outer tube and the reactor effluent through the inner tube, the feedstock is pre-heated before entering the reactor zone. They operated SCWG of 5 wt.% glycerol-water solution at 580 °C and 270 bar. Elliott et al. (2004) designed a scaled-up reactor based on a bench-scale continuous flow design. The scaled-up reactor was operated with 10 L/h feedstock at T=350 °C and 24 MPa. In this design, the feedstock was pumped by a high-pressure reciprocating plunger pump into a double-tube heat exchanger with a total length of 17 m, which preheats the feedstock to 100 °C. Three different feedstocks were examined in this reactor, dairy manure, Midwest Grain Products; distillers' dried grains and solubles (DDG&S). While they achieved high levels of methane, many

processing difficulties were observed in the fixed bed tubular reactor including reactor plugging.

2.5. Conclusions

Supercritical water gasification is a viable option for converting high water content biomass into valuable gases including methane and hydrogen. In the case of using short residence times and high temperatures, hydrogen is the dominant product. High amounts of methane gas are expected at low SCW temperatures based on thermodynamic equilibrium calculations, but the gasification efficiency is generally low without using a catalyst. Utilizing a proper catalyst is essential to enhance the methanation reaction. Nickel and ruthenium supported on alumina and carbon are highly active catalysts for both methanation and the water-gas shift reaction, depending on operational conditions. Ruthenium might also be used as a promoter to enhance the catalytic activity of nickel catalysts. A high loading of nickel on a supported catalyst generally favors methane formation, but there is also usually an optimal loading concentration.

To improve the hydrogen production yield, addition of alkali salts and high temperatures are favorable. However, to maintain a high hydrogen yield, the substrate concentration should be maintained low. The SCWG process can be further improved by measures such as enhancing heat exchange efficiency to decrease energy costs and optimizing the process conditions including designing more active and stable catalysts.

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CHAPTER 3. SCREENING OF METAL CATALYSTS AND SUPPORTS FOR METHANE AND HYDROGEN PRODUCTION FROM GLUCOSE VIA SUPERCRITICAL WATER GASIFICATION

3.1. Introduction

Supercritical water (SCW) refers to an state of water which is no longer a liquid or gas. When water reaches its critical point, 374 °C and 22.1 MPa, its properties change drastically: diffusivity increases, viscosity decreases, the solubility of organic compounds improves greatly while the solubility of inorganic compounds decreases (Elliott, 2008). All these advantages make SCW a unique media which can dissolve organic compounds while enhancing their conversion into gas products. SCW is not only a medium, but also can act as a reactant, participating in the steam reforming reactions, for example (Zhang et al., 2011). Among all the hydrothermal processes, supercritical water gasification (SCWG) is the only viable way to convert high water content biomass or waste water slurries (even > 90 wt.%) into green fuels without pre-drying. The potential of this process to convert aqueous organic matter into high calorific gases such as hydrogen or methane makes this a promising alternative for generating syngas or synthetic natural gas (SNG) (Matsumura et al., 2005). Hydrothermal processes have emerged since 1978 by Modell at Massachusetts Institute of technology (MIT). Since then many researchers e.g. University of Hawaii, Osaka Gas, Pacific Northwest National Laboratory, Forschungszentrum Karlsruhe (FzK), Hiroshima University, University of Twente, and BTG Company, have investigated the development of SCWG to pilot and large scales. Although, these research programs are on-going, only a very limited number of large-scale reactors have been built, at FzK for instance, with a capacity of 100 L/h and at the University of Twente with a 30 L/h capacity (Mozaffarian et al., 2004).

Typically the gas product composition is directly influenced by the type of feedstock, reactor design, operating conditions, and choice of catalyst. The main gas products are typically methane, hydrogen, carbon dioxide, carbon monoxide, water vapor, and a low concentration of C₂-C₃. However, the proportion of these gases can vary from a methane rich gas to a hydrogen rich gas based on the temperature (Kruse, 2008). In the low SCWG temperature zone, 374 to

500 °C, methane is the thermodynamically favored gas product (Castello and Fiori, 2011). The presence of a catalyst, however, is essential (Osada et al., 2006). Heterogeneous catalysts have the advantages of high selectivity, recyclability, environment-friendly in comparison to homogenous catalyst (Guo et al., 2010). Rh, Ru, and Ni are reported to be the most stable and effective heterogeneous catalysts for SCWG of organics (Elliott et al., 1993). Although Ni is less stable than Ru, it is a much lower cost effective catalyst than noble metals. Ruthenium metal catalyst showed complete carbon conversion into gases from wet dairy manure (Elliott et al., 2004). Ru/TiO₂ showed a high selectivity towards methane formation of SCWG of cellulose and lignin at T= 400 °C (Osada et al., 2003). A solution of 0.6 M glucose was almost completely gasified in the presence of 16 wt.% Ni/AC at 575-725 °C (Lee and Ihm, 2008). Recently, many groups have been investigating SCWG of model compounds. The greatest challenge in up-scaling SCWG processes is the problem of reactor plugging, mainly caused by char agglomeration in the heated part of the flow type reactor system (Lu et al., 2006).

Ruthenium and nickel were chosen for this research as they are highly active and stable under the harsh conditions of supercritical water (Elliott and Sealock, 1996). Moeller and Bartholomew (1982) reported that Ni-Ru catalyst is extremely efficient in suppressing carbon deposition. Nickel and ruthenium also have an excellent potential to promote methanation reactions (Lee and Ihm, 2008; Sealock et al., 1988). They may, however, also promote reactions leading to hydrogen production depending on the operating conditions (Byrd et al., 2007a; Elliott et al., 2004). Moreover, ruthenium has been shown to be a very effective co-catalyst to nickel even at concentrations as low as 1 wt.% (Elliott and Sealock, 1988; Zhang et al., 2011b).

In this research, different catalyst supports with various nickel-ruthenium loadings were studied for supercritical water gasification of glucose as the model biomass compound. The experiments were carried out at a relatively low temperature using a flow type reactor. Different nickel and ruthenium catalysts supported on γ -Al₂O₃, TiO₂, and AC support were studied for SCWG of the model compound. Extended runs to 20 hour time on stream were carried out to explore the catalyst stability. Low catalytic activity and frequent plugging occurred after only 3 hours on-stream for nickel-ruthenium on either titanium oxide or activated carbon, respectively. SEM-EDX, Pulse Chemisorption, and XRD analysis were performed to explore the effects of ruthenium as a co-catalyst or promoter.

3.2. Materials and methods

3.2.1. Feedstock and catalyst preparation

A glucose-water solution was prepared by dissolving α -D-glucose (Sigma Aldrich) in distilled water to reach a concentration of 50 g/L. Catalysts were prepared by the incipient wetness impregnation or co-impregnation of the metals on three different supports (Lee and Ihm, 2008). Water-soluble metal salts including nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$) and ruthenium (III) nitrosyl nitrate solution in dilute nitric acid ($\text{HN}_4\text{O}_{10}\text{Ru}$), supplied by Sigma-Aldrich, were used in the impregnation. The support materials were γ - Al_2O_3 (from Inframat Advance Materials), TiO_2 (Sigma-Aldrich), and activated carbon (AC). The AC used in this study was a biomass-derived AC prepared in-house from pine wood sawdust. Details of this catalyst and preparation method are summarized elsewhere by Zhang et al. (2011a). All of the catalysts were calcined in air at 600° C (10° C/min heating rate) for 6 hours. After cooling, the catalysts were crushed and sieved to a nominal average diameter of 575 μm (sieves with mesh size 300-850 μm , ACS). Temperature-programmed-reduction (TPR) from Micromeritics (AutoChem II) with 10° C/min heating rate up to 900° C under 50 ml/min H_2/Ar gas flow ($v/v=1:9$) was utilized to measure the temperature reduction of catalysts. Before TPR method, each catalyst was oxidized by temperature programmed oxidation (TPO) up to 750 °C with the same heating rate to saturate all nickel particles with oxygen. A summary of the BET surface area (by Tristar II3020 instrument) for catalysts are represented in the Table 3.1.

Table 3.1 - Catalyst compositions and physical characteristics

Catalyst	Metal content (wt.%)	Support	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)
Ni _{30%} Ru _{2%} /γ-Al ₂ O ₃	30% Ni+2% Ru	γ-Al ₂ O ₃	110.1	0.27	9.88
Ni _{20%} Ru _{2%} /γ-Al ₂ O ₃	20% Ni+2% Ru	γ-Al ₂ O ₃	126.5	0.29	9.23
Ni _{10%} Ru _{2%} /γ-Al ₂ O ₃	10% Ni+2% Ru	γ-Al ₂ O ₃	139.5	0.36	10.4
Ni _{20%} /γ-Al ₂ O ₃	20% Ni	γ-Al ₂ O ₃	113.2	0.31	10.82
Ru _{2%} /γ-Al ₂ O ₃	2% Ru	γ-Al ₂ O ₃	152.2	0.44	11.54
γ-Al ₂ O ₃ (catalyst support)	Na ¹	na	154.1	0.42	11.02
Ni _{20%} Ru _{2%} /TiO ₂	20% Ni+2% Ru	TiO ₂	27.9	0.14	20.6
Ni _{10%} /AC ²	10% Ni	AC	1.1×10 ³	0.68	2.4

¹ na : not applicable² Ref (Zhang et al., 2011b)

3.2.2. Apparatus and experimental procedure

A schematic diagram of the supercritical water gasification reactor is represented in Figure 3.1. The experiments in this research were performed using a 9.55mm OD×6.34mm ID×472 mm length continuous-flow tubular reactor constructed from Inconel 625. Crushed and sieved catalyst was packed in the tube while supported on a porous stainless steel filter (mesh 80). To minimize the possible carry-away of catalyst particles, a small amount of quartz wool (1cm depth) was placed on the support screen before the catalyst was added. The packed reactor was heated in an electrical furnace to the reaction temperature. The feedstock, 5 wt.% aqueous glucose solution, was pumped into the reactor from the top by a high pressure liquid metering pump from Eldex (optos series). The feed rate was kept constant at 1mL/min which translates to

WHSV=3 h⁻¹ (weight hourly space velocity, the flow-rate of reactant per mass of catalyst) throughout the experiments. In All tests in this study, temperature was held constant at 500 °C, and pressure in the system was maintained at 4000 psi (~27.5 MPa) via a back-pressure regulator located downstream of the reactor. For most runs, the experiments were operated for at least 6 hours on stream at a time. A few tests for 20 hour on-stream were also carried out over three days to examine the stability of the selected catalysts in SCWG.

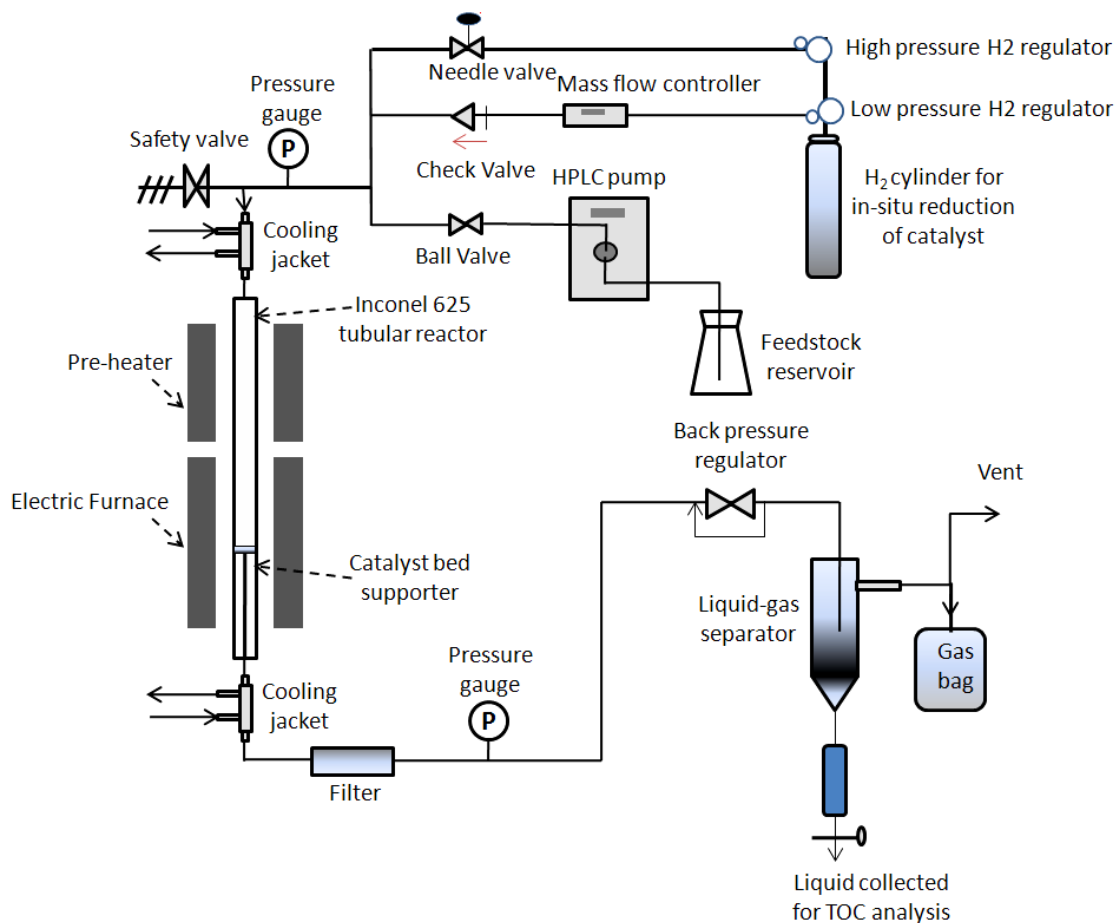


Figure 3.1 - Schematic diagram of the bench scale flow type reactor

3.2.3. Gas and liquid product analysis:

For each experiment, both the gas and liquid products were collected periodically in a gas bag and sample vial, respectively. To measure the exact volume of the gas in the sample bag, a known volume of nitrogen was injected into the sample bag as an internal standard. The gas samples were analyzed by Micro-GC (Agilent 3000A, Cerity software) equipped with dual

columns (MS and PLOT-Q) and TCD (thermal conductivity) detectors. The total organic carbon (TOC) content of liquid effluents was analyzed using a Shimadzu TOC-V CPH instrument. Catalyst stability was verified by Inductively Coupled Plasma (ICP) (Optima3000, PerkinElmer) analysis to determine how much, if any, of the catalyst metals had been leached out during the reaction.

3.2.4. Tar and char analysis

While char refers to unconverted biomass, tar is the byproduct of undesired side reactions (Calzavara et al., 2005). After each experiment, the tarry by-products were collected from the reactor after it was cooled to room temperature by washing with A.C.S. reagent-grade ethyl acetate solvent to collect all water-insoluble organic compounds. The resulting brown liquid was allowed to separate into two phases using a separatory funnel. The organic phase (the solvent) was evaporated using a rotary evaporator at 60 °C under vacuum. The remaining viscous liquid is referred to as tar. The elemental composition (C, H, and O) of the tar was determined by elemental analysis on a Flash EA 1112 series CHNS-O analyzer. To evaluate char production, the spent catalyst was analyzed on a thermogravimetric analyzer (TGA), High Temp DTA/TGA Rheometer, SDT Q600 from TA Instruments. Samples of the spent catalyst were heated to 900 °C under a 40 mL/min air flow rate at ambient air pressure with 10 °C/min heating rate. Scanning Electron Microscopy coupled with Energy Dispersive X-ray (SEM/EDX) Spectroscopy (SEM-EDX) analysis, which is a Physical Electronics Model PHI 660 instrument was used to examine the deposition of organic residues on the catalyst.

3.3. Definitions

The yield for each component, for instance methane, is defined by the following equations:

$$\text{Methane yield (mol/mol)} = \frac{\text{Moles of CH}_4 \text{ recovered in gas}}{\text{Total moles of carbon fed}} \quad (\text{Eq. 3.1})$$

Since the total carbon in the gas product comes dominantly from methane, carbon dioxide, and carbon monoxide, carbon gasification efficiency is defined as the total carbon yield of the gas phase.

$$\text{Carbon gasification efficiency (mol/mol)} = \frac{\text{Moles of carbon recovered in gas}}{\text{Total moles of carbon fed}} \quad (\text{Eq. 3.2})$$

For char and tar production, yields are defined as follows:

$$\text{Tar yield (wt.\%)} = \frac{\text{Total mass of carbon from tar recovery}}{\text{Total mass of carbon fed}} \times 100\% \quad (\text{Eq. 3.3})$$

$$\text{Char yield (wt.\%)} = \frac{\text{Total mass of char recovered}}{\text{Total mass of carbon fed}} \times 100\% \quad (\text{Eq. 3.4})$$

3.4. Results and discussion

3.4.1. Non-catalytic supercritical water gasification

For better understanding of a role of the catalyst in supercritical water gasification of an organic compound, several preliminary experiments were carried out in the absence of catalyst (blank tests) under conditions of 500 °C, 27.5 MPa, and a WHSV of 3 h⁻¹. The 5 wt.% glucose-water solution was fed into the reactor at 1mL/min. The results are shown in Figure 3.2. Over the course of 7 hours, at steady state only 0.13 mol of carbon containing gaseous products (dominantly CH₄, CO, CO₂) was produced from every mol of carbon fed into the reactor. Only 0.1 mol hydrogen/mol carbon-fed and almost no methane were formed, suggesting the necessity of a suitable catalyst for SCWG at such operating conditions.

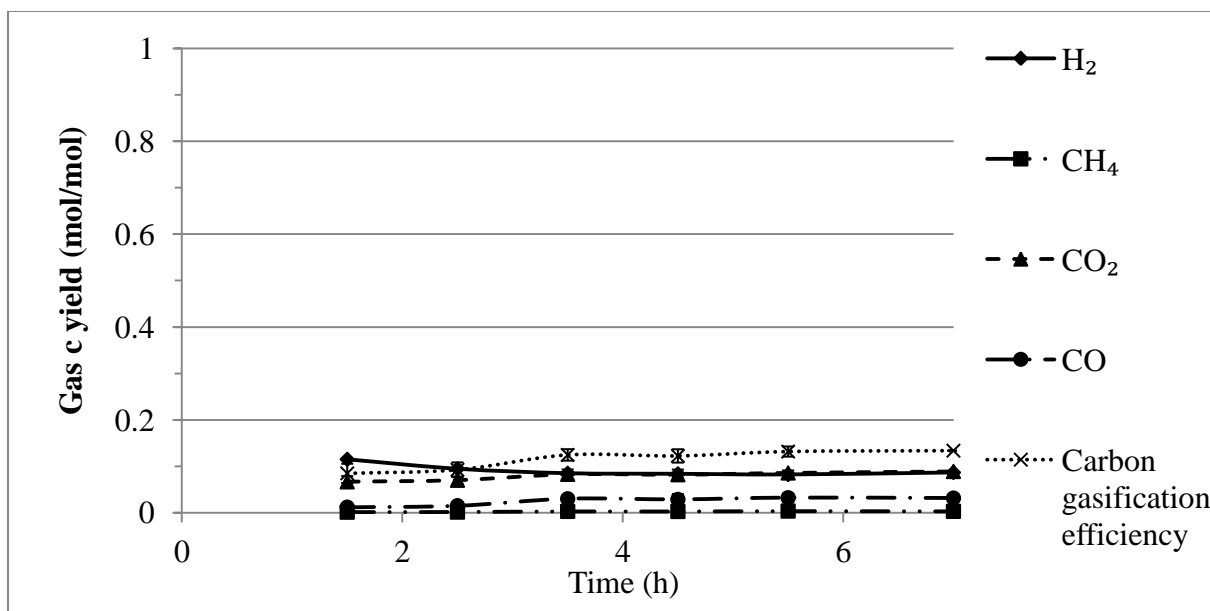


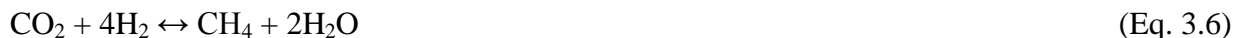
Figure 3.2 - Gas yields from SCWG of 5 wt.% glucose-water solution without any catalyst (blank test) at 500 °C and 27.5 MPa at WHSV of 3 h⁻¹.

The first gas sample was collected after 1.5 hours on stream, and then monitored for stability for up to 7 hours showing very little changes in the measured gas production. The virtual absence of methane in the blank test, and the tar yield as high as 17 wt.% are the evidence for the necessity of a catalyst. In addition to improving gasification efficiency, catalysts can suppress tar formation which is one of the major challenges in supercritical water gasification processes (Byrd et al., 2007b).

3.4.2. Effect of different metal catalysts

Glucose begins to decompose into a brownish colored substance at temperatures approaching its melting point, and above 240 °C it decomposes into compounds such as fructose, dihydroxyacetone, glyceraldehydes, erythrose, glycolaldehyde, pyruvaldehyde, 1,6 anhydroglucose, acetic and formic acid, and 5-HMF (Kabyemela et al., 1999; Örsi, 1973). Hence, the choice of catalyst plays an important role in gasifying of not only the glucose but its decomposition byproducts, as well as in inhibiting the reaction pathways which may lead to tar production.

The product distribution and carbon gasification efficiency for the gas products (H₂, CH₄, CO₂, CO) in the presence of different metal catalysts with various metal loadings (Ni, Ru) on γ -Al₂O₃ and TiO₂ support in SCW at 500 °C and 27.5 MPa for 6 hour time on-stream is shown in Figure 3.3. As expected, the non-catalytic reaction has the lowest gas yield. With the Ni_{20%}/ γ -Al₂O₃ catalyst, it produced 0.54 mol H₂ and 0.12 mol CH₄ per mole carbon fed, which suggests that the catalyst is very active for hydrogen production but less effective for methane production. This catalyst was also able to decrease tar formation to as low as 3.11 wt.% in comparison with 17.33 wt.% tar yield in the blank test (Table 3.4). However, incomplete gasification of the feedstock was observed with only 0.71 mol/mol carbon gasification efficiency. On the other hand, Ru_{2%}/ γ -Al₂O₃ showed very poor activity for SCWG of glucose, with carbon gasification efficiency of only ~0.12 mol/mol and negligible reduction in tar yield (Table 3.4). Compared with the blank test, the Ru_{2%}/ γ -Al₂O₃ catalyst suppressed the formation of CO while promoted the formation of methane. It may suggest the capability of the Ru catalyst to catalyze the methanation reactions via Eq. 3.5 and Eq. 3.6.



Interestingly, adding 2 wt.% ruthenium metal to Ni_{20%}/ γ -Al₂O₃ catalyst to prepare Ni_{20%}Ru_{2%}/ γ -Al₂O₃, resulted in a significantly enhanced carbon gasification efficiency to be 0.98 mol/mol, i.e., it was able to almost completely gasify all carbon in the glucose-water solution into gases. The Ni_{20%}Ru_{2%}/ γ -Al₂O₃ catalyst also produced the highest methane yield of 0.5 mol/mol carbon-fed, accompanied by no formation of CO and greatly reduced hydrogen yield (0.25 mol/mol carbon-fed) in comparison with those of Ni_{20%}/ γ -Al₂O₃ catalyst, suggesting the addition of 2% Ru to Ni_{20%}/ γ -Al₂O₃ promotes not only carbon gasification efficiency, but also methane formation likely via the methanation reaction of CO and H₂ (Eq. 3.5). Comparing the performance of all three catalysts (Ni_{20%}/ γ -Al₂O₃, Ru_{2%}/ γ -Al₂O₃ and Ni_{20%}Ru_{2%}/ γ -Al₂O₃), it is clear that the presence of a small amount of Ru in the Ni_{20%}Ru_{2%}/ γ -Al₂O₃ catalyst functions as a catalyst promoter to enhance the activities of the Ni catalyst for both carbon gasification efficiency and methane formation. Similar results were obtained by the authors' group previously in SCWG of glucose at 600 °C and 24 MPa for hydrogen production (Zhang et al.,

2011b). Ruthenium as a Ni catalyst promoter may play a critical role in improving nickel catalyst dispersion and catalyst reducibility, which will be discussed later in this paper.

The $\text{Ni}_{10}\text{Ru}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst achieved the highest H_2 gas yield (0.68 mol/mol carbon-fed) in this study. However, this catalyst only converted 0.63 mol/mol of carbon in the feedstock into carbon-containing gaseous products, and produced much less methane (0.14 mol/mol carbon-fed) than $\text{Ni}_{20}\text{Ru}_2/\gamma\text{-Al}_2\text{O}_3$ (~0.5 mol CH_4 /mol carbon-fed). When further increasing Ni loading from 20% to 30% for the $\text{NiRu}/\gamma\text{-Al}_2\text{O}_3$ catalysts, H_2 yield slightly increased while both the carbon gasification efficiency and methane yield reduced. As such, it may be concluded that nickel loading significantly influence the carbon gasification and the gas product distribution. In the presence of 2 wt.% Ru, 10 wt.% Ni produced the highest yield of H_2 , while 20 wt.% Ni seems to be the optimal Ni loading for methane yield and carbon gasification efficiency. The effect of metal loading will be further discussed in a later section of this paper.

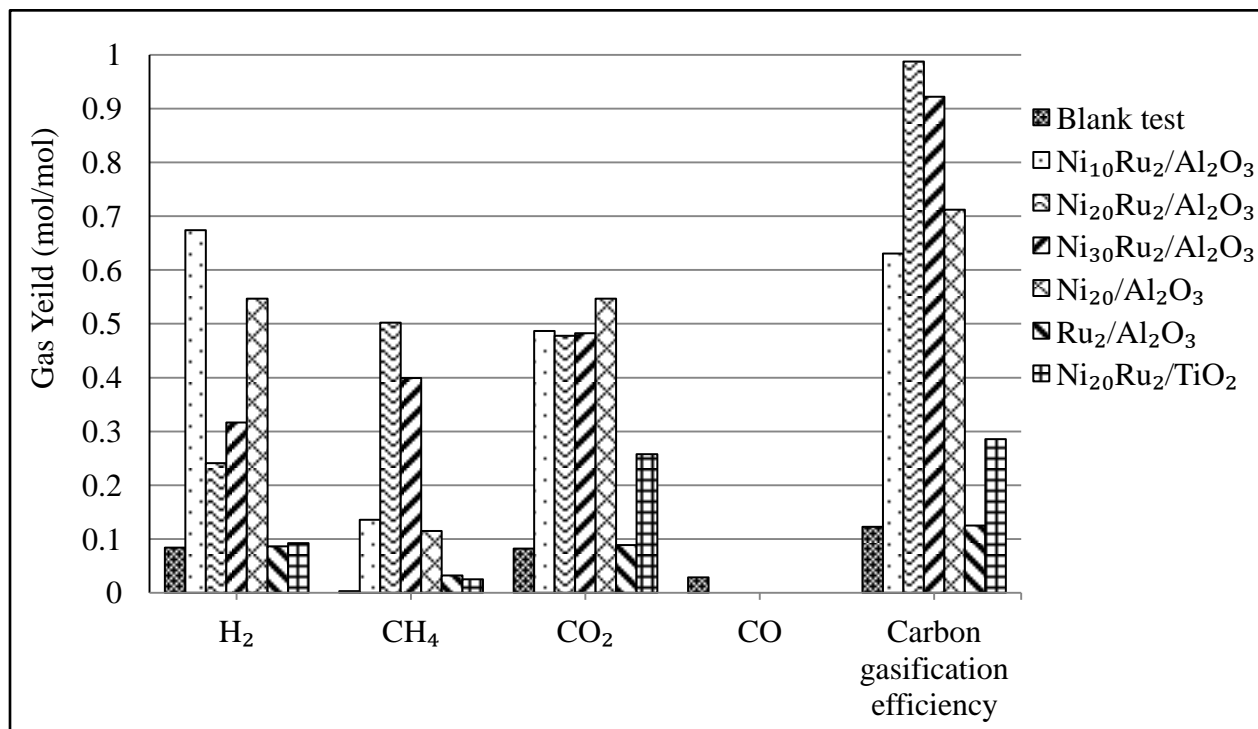


Figure 3.3 - Gas composition and total carbon containing gases yields from SCWG of 5 wt.% glucose-water solution at 500 °C and 27.5 MPa with $\text{WHSV}=3 \text{ h}^{-1}$ (two trials for each experiment confirm less than 3% error. To prevent disorderly error bars are not represented on the graph)

As shown previously in Table 3.1 the BET surface areas for different catalysts follow the following trend: $\text{Ni}_{10\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3 > \text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3 > \text{Ni}_{30\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$, while the greatest carbon gasification efficiency was achieved by $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ followed by $\text{Ni}_{30\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Ni}_{10\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$. Thus catalytic activity is not directly related to the BET surface area of the catalyst.

γ -alumina is widely used as a catalyst support for hydrothermal gasification of biomass or model compounds (Elliott et al., 1993). Titanium (II) oxide was also studied here to investigate the effect of catalyst support on SCWG of the model compound. The results showed that TiO_2 was not a very effective support for $\text{Ni}_{20\%}\text{Ru}_{2\%}$, probably because titanium converted from anatase to rutile phase form during calcinations at 600 °C. The carbon gasification efficiency of $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ was more than three times greater than that of the $\text{Ni}_{20\%}\text{Ru}_{2\%}/\text{TiO}_2$. This may be due, in part, to the difference in surface area. The BET surface area for the $\text{Ni}_{20\%}\text{Ru}_{2\%}/\text{TiO}_2$, was less than 25% that of the $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ catalyst ($27.9\text{m}^2/\text{g}$ vs. $126.5\text{m}^2/\text{g}$). The difference may also be due to the interaction of catalyst metals with the support, as TiO_2 particles may migrate onto the nickel surface which may geometrically blocks active sites (Bradford and Vannice, 1996).

In addition to the alumina and titanium (II) oxide supported catalysts, an activated carbon support with higher BET surface area ($>1000\text{ m}^2/\text{g}$) (Table 3.1) was prepared and tested under the same conditions as the other catalysts. Unfortunately this catalyst caused rapid tar build-up and the reactor repeatedly plugged after only 3 hours on-stream. Therefore, no valid data were obtained using the AC supported catalyst.

To investigate the benefits and possible roles of ruthenium metal as a co-catalyst in Ni catalyst, $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ catalyst was compared with $\text{Ni}_{20\%}/\gamma\text{-Al}_2\text{O}_3$. It has been demonstrated that nickel catalyst is drastically more active in the SCWG of glucose in reduced metal form, whereas ruthenium activity is almost the same for both metallic and oxidized form (Zhang, 2011a). Figure 3.4 provides the temperature-programmed-reduction (TPR) profiles of fresh catalyst of both $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Ni}_{20\%}/\gamma\text{-Al}_2\text{O}_3$. It can be seen in the Figure 3.4 that the temperature required for reduction of NiO in $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ catalyst (420 °C peak temperature) is significantly lower than that (460 °C peak temperature) of the $\text{Ni}_{20\%}/\gamma\text{-Al}_2\text{O}_3$.

Hence, by adding 2 wt.% noble metal of ruthenium to nickel catalyst on γ -Al₂O₃ significantly promote the reducibility of NiO. The main role of Ru in the supported Ni catalyst systems was believed to be to decrease the reduction temperature of nickel oxide followed by the formation of Ni_xRu_{1-x} solid solution. Similar effect was observed for the Cu promoted Ni catalyst systems (Yakovlev et al., 2009). Interactions between Ni²⁺ and alumina may result in different phases being formed including NiO and NiAl₂O₄ (Li et al., 2006). The second phase is more stable and is the main reason for stability of the nickel catalyst. However, it is hard to reduce NiAl₂O₄ at temperatures below 700° C (Castro and Iriarte, 2008; Koo et al., 2008). From Figure 3.4, the NiAl₂O₄ reduction peak for Ni_{20%}/γ-Al₂O₃ catalyst may be present at 620 °C while this peak may be present at 740° C for Ni_{20%}Ru_{2%}/γ-Al₂O₃ catalyst. The smaller peak of NiAl₂O₄ in the Ni_{20%}Ru_{2%}/γ-Al₂O₃ confirms that ruthenium helps reduce the formation of inactive NiAl₂O₄ and increases the dispersion of nickel oxide on the alumina surface (Koo et al., 2008).

Since the media in SCWG is water, catalyst can become oxidized in this high temperature environment. However, the lower reduction temperature found for the mixed metal catalyst means that the reduction of the oxidized nickel could be readily achieved by in-situ reduction with the H₂/CH₄ produced at the reaction conditions. With this, the catalyst can stay active during the course of the SCWG experiments

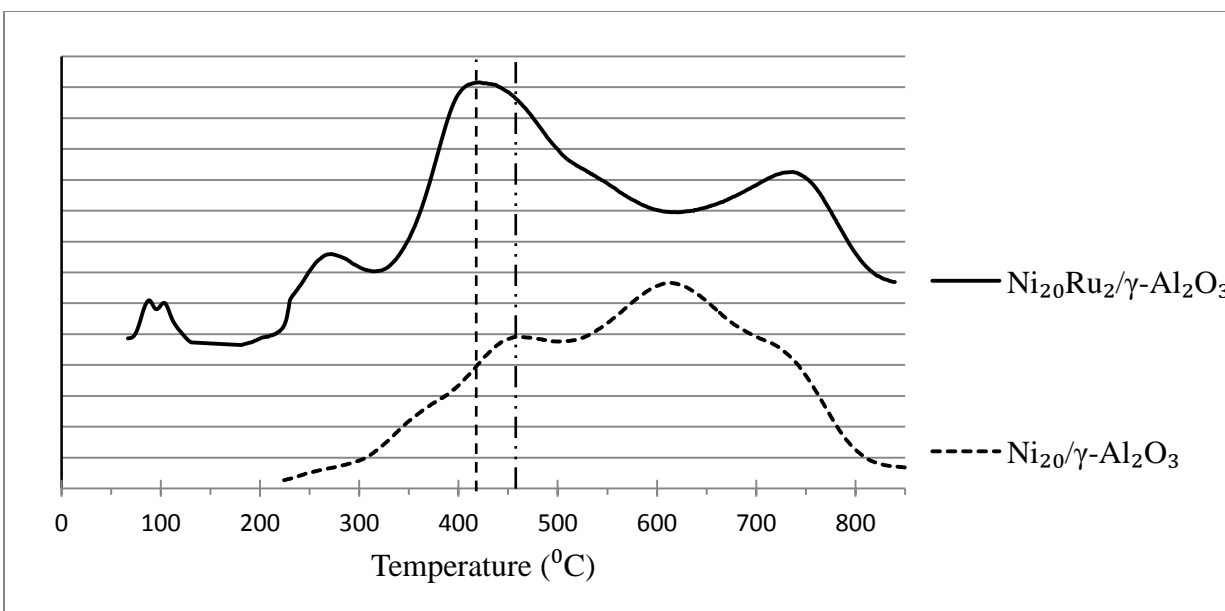


Figure 3.4 - TPR analysis results for fresh $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Ni}_{20\%}/\gamma\text{-Al}_2\text{O}_3$ catalysts (catalysts were pre-oxidized by TPD up to 750 °C with a heating rate of 10 °C/min).

H_2 pulse chemisorption analysis for the fresh catalysts of $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Ni}_{20\%}/\gamma\text{-Al}_2\text{O}_3$ are summarized in the Table 3.2. This table shows the effect of ruthenium metal addition on nickel metal dispersion. Nickel dispersion is 3.3 for $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ with a metallic surface area of 4.4 m^2/sample while these values are 1.2 and 1 m^2/sample , respectively, for $\text{Ni}_{20\%}/\gamma\text{-Al}_2\text{O}_3$. Therefore with the addition of a small amount of Ru, the dispersion of nickel increase to more than doubles, and the metallic surface area was also highly promoted. These data are in a good agreement with the BET analytical results for the $\text{Ni}_{20\%}/\gamma\text{-Al}_2\text{O}_3$ as compared with the $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ (Table 3.1). It should be mentioned that higher dispersion translates to better catalyst stability and a lower risk for nickel particle sintering (Li et al., 2006).

Table 3.2 - H₂ pulse chemisorption results for fresh Ni_{20%}Ru_{2%}/γ-Al₂O₃ and Ni_{20%}/γ-Al₂O₃ catalysts

	Ni _{20%} /γ-Al ₂ O ₃	Ni _{20%} Ru _{2%} /γ-Al ₂ O ₃
Metal Dispersion (%)	1.2	3.3
Metallic Surface Area (m ² /g)	1.0	4.4
Metallic Surface Area (m ² /g metal)	8.0	22.
Active Particle Diameter (hemisphere, nm)	80.5	30.4
Cubic crystallite size (nm)	67.1	25.3

Table 3.3 presents the ICP results from both fresh and spent Ni_{20%}Ru_{2%}/γ-Al₂O₃ and Ni_{20%}/γ-Al₂O₃ catalysts. The Ni_{20%}/γ-Al₂O₃ shows evidence of leaching after 6 hours on-stream. It is expected that longer time on-stream will decrease the catalytic activity of Ni_{20%}/γ-Al₂O₃. In contrast, the Ni_{20%}Ru_{2%}/γ-Al₂O₃ catalyst remained highly stable even after 20 hours on-stream. This table also confirms the necessity of ruthenium as co-catalyst not only to increase nickel dispersion but also to stabilize the nickel loaded onto γ-alumina. Figure 3.5 shows the yields of all gas species were fairly stable after 6 hours on-stream from SCWG of glucose at 500 °C in the presence of Ni_{20%}Ru_{2%}/γ-Al₂O₃ catalyst. The results of the extended stability test for 20 hour time on-stream, carried out under the same conditions, will be presented and discussed in the next section of this paper.

Table 3.3 - ICP results for fresh and used Ni_{20%}Ru_{2%}/γ-Al₂O₃ and Ni_{20%}/γ-Al₂O₃.

Element	Mass of element/Mass of catalyst (g/g)			
	Ni _{20%} Ru _{2%} /γ-Al ₂ O ₃ (fresh)	Ni _{20%} Ru _{2%} /γ-Al ₂ O ₃ (20 h)	Ni _{20%} /γ-Al ₂ O ₃ (Fresh)	Ni _{20%} /γ-Al ₂ O ₃ (6 h)
Al	0.14	0.14	0.13	0.03
Ni	0.12	0.13	0.12	0.07

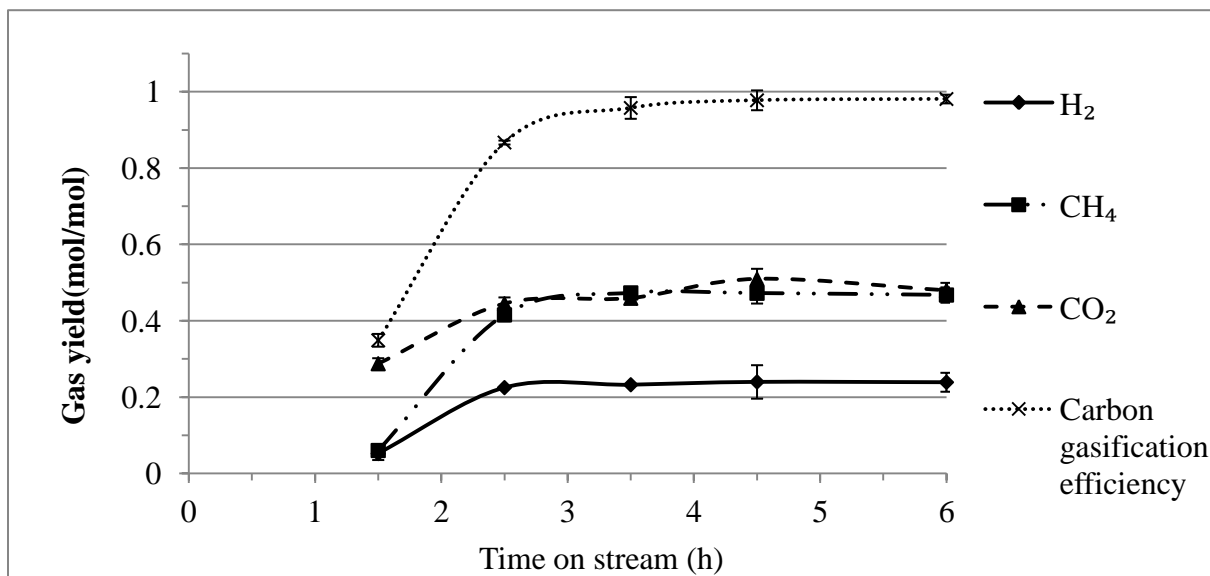


Figure 3.5 - Gas composition and total carbon containing gas yields from SCWG of 5 wt.% glucose-water solution at 500 °C and 27.5 MPa, with WHSV=3 h⁻¹ in the presence of Ni_{20%}Ru_{2%}/γ-Al₂O₃ catalyst

3.4.3. Stability tests on Ni_{20%}Ru_{2%}/γ-Al₂O₃

To investigate the stability of the best catalyst, i.e., Ni_{20%}Ru_{2%}/γ-Al₂O₃ selected based on the results as discussed above, experiments were conducted for an extended length of time (20 h) under the same conditions as the previous experiments. Such tests were carried out over the course of three days, 8 hours for the first day, 6 hours for the second and third day, respectively. The results of the first 8 hours of the extended experiment were found to be in a good agreement with the previous results from the 6-h catalyst screening tests. No plugging or deactivation of the catalyst was observed for the second or third days of the run. Figure 3.6 shows the yields and composition of gas products from SCWG of 5 wt.% glucose-water solution at 500 °C and 27.5 MPa, with WHSV= 3 h⁻¹, in the presence of Ni_{20%}Ru_{2%}/γ-Al₂O₃ catalyst for 20 hour time on-stream (stability test). As shown from the figure, the catalyst remained its high activity for the whole duration of the tests (20 hours), leading to approx. 1 mol/mol carbon gasification efficiency without any indication of deactivation. Almost zero TOC values were measured for the liquid effluents, which also confirm that near complete

carbon conversion was achieved. Only a negligible portion of the carbon from the feedstock was converted into char and tar. These results demonstrate superb stability for the catalyst under the harsh conditions of SCWG.

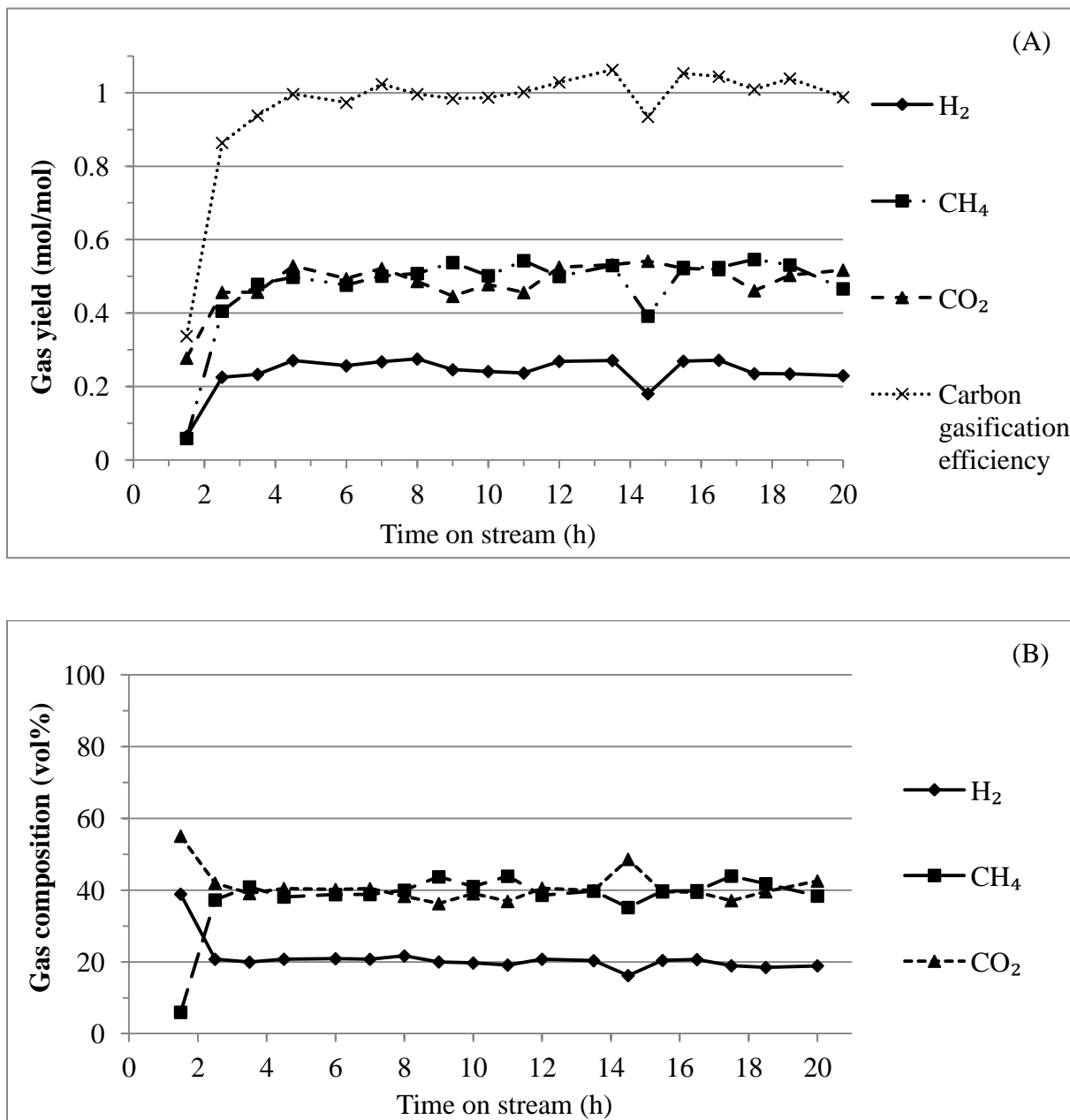


Figure 3.6 - Yields (A) and composition (B) of gas products from SCWG of 5 wt.% glucose-water solution at 500 °C and 27.5 MPa, with WHSV= 3 h⁻¹, in the presence of Ni_{20%}Ru_{2%}/γ-Al₂O₃ catalyst for 20 hour time on-stream (stability test).

The most common problem in continuous reactors is plugging which results from the accumulation/agglomeration of tar and char on the catalyst particles. Other common problems in flow type reactors with heterogeneous catalysts include sintering of catalyst particles (occurring at high temperatures), decomposition of the support material and leaching of the catalyst metals. All of these would decrease the catalytic activity. In order to predict the above-mentioned problems for the selected catalyst, Ni_{20%}Ru_{2%}/γ-Al₂O₃, the fresh and used catalysts of Ni_{20%}Ru_{2%}/γ-Al₂O₃ were characterized using XRD, TGA and SEM-EDX. The results of the catalyst characterizations are discussed as follows.

The XRD patterns for fresh and spent Ni_{20%}Ru_{2%}/γ-Al₂O₃ catalyst are illustrated in Figure 3.7. In the fresh catalyst, nickel and ruthenium are presented in their oxidized form (NiO and RuO₂). However, these metals were detected in their metallic forms after 6 hours on stream. This is attributed to *in-situ* reduction of the catalysts before each experiment and the in-reaction reduction by the reducing gas products (H₂ and CH₄). The metallic form of nickel particles are actually the active sites for the SCWG of glucose (Zhang et al., 2011b). Based on these XRD patterns, it can be concluded that nickel and ruthenium remain in metallic form after 6 hours glucose SCWG at 500 °C and these metallic forms of Ni/Ru are responsible for the high activity of Ni_{20%}Ru_{2%}/γ-Al₂O₃ catalyst. The XRD patterns for the spent catalyst also contain a strong peak at 2θ~26°, ascribing to the diffraction lines of crystalline carbon. This implies char/coke deposition on the spent Ni-Ru catalyst, which can be further evidenced by TGA and SEM-EDX as discussed below.

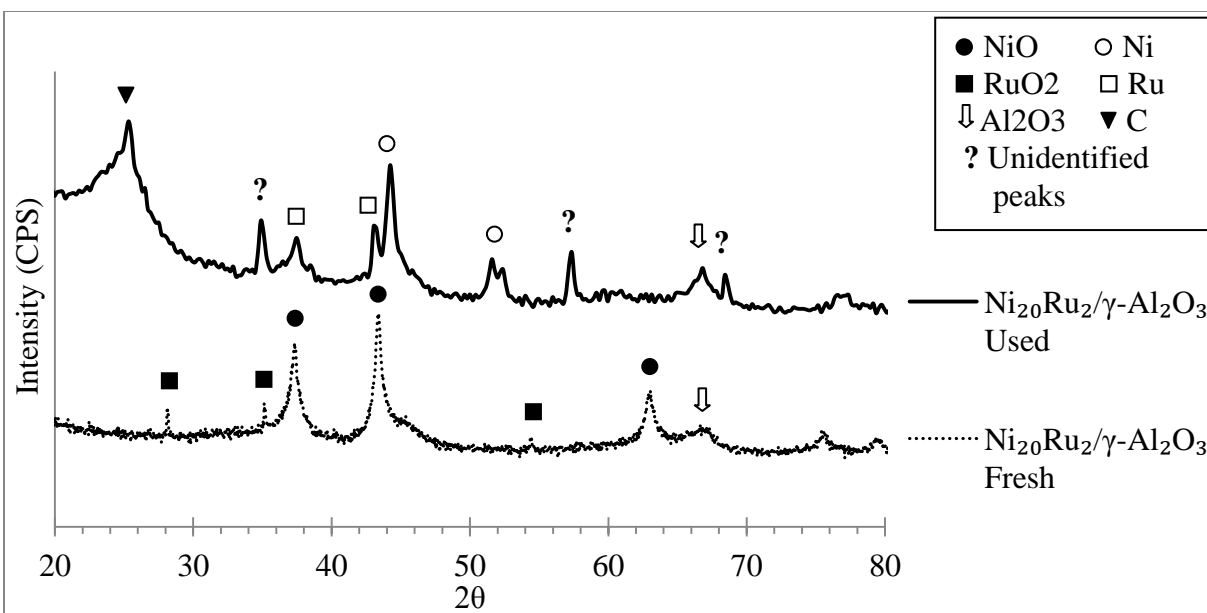


Figure 3.7 - XRD patterns for fresh and used $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ after 6 hour time on stream at 500 °C

The spent $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ catalysts after 6 and 20 hours on stream were analyzed by TGA to quantify the char formation (or coke deposition) during the experiments. Figure 3.8 displays the thermogravimetry (TG) profiles. Oxidizable amorphous carbonaceous species and water are responsible for the mass loss below 300 °C, whereas the mass loss at higher temperatures are ascribed to coke oxidation to CO and CO₂ (Koo et al., 2008). Zhang et al. (2011b) demonstrated that ruthenium promoter on the $\text{Ni}_{10\%}\text{Ru}_{1\%}/\gamma\text{-Al}_2\text{O}_3$ catalyst was responsible for decreased char/tar formation. The carbon burned off at lower oxidation temperatures can be ascribed to the presence of filamentous and amorphous forms of carbon. However, the carbon burned off at higher temperatures is more likely present in a graphite-like crystalline form (Wang and Lu, 2000). The presence of the latter form of carbon on the catalyst may cover the catalyst active sites and reduce its activity, which may result in increased char/tar formation. It can be seen from Figure 3.8 that the Ni-Ru catalyst contained only 23 wt.% char after 6 hours on stream, and that this value increased to 50 wt.% after 20 hours on-stream. As shown previously, the catalyst remained its high activity after 20 hours, so the char formation and accumulation in the reactor did not appear to deactivate this catalyst.

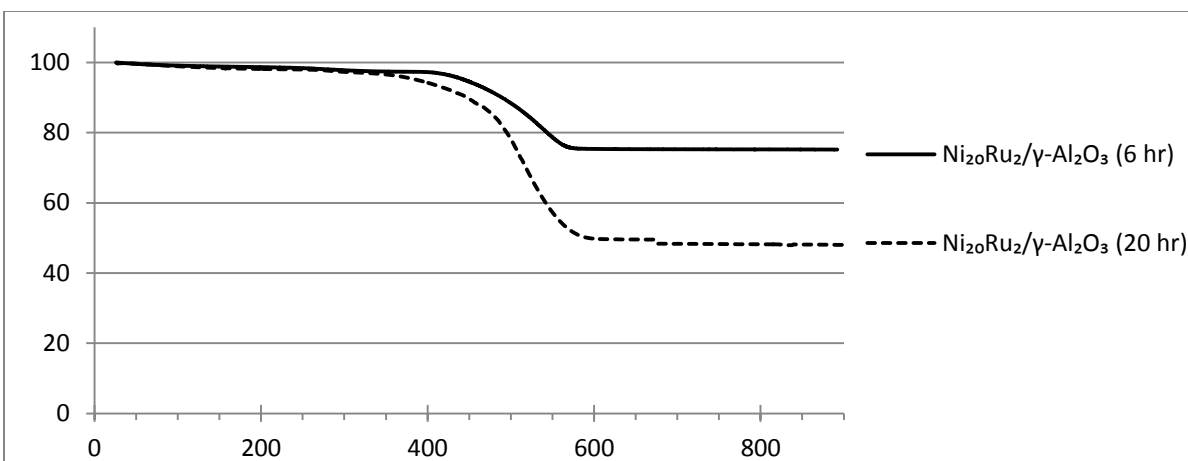


Figure 3.8 - TGA profiles for $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ after 6 and 20 hour time on stream under air atmosphere.

The SEM-EDX analysis results of the fresh (not reduced) and spent (after 20h on-stream) $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ catalyst are presented in Figure 3.9. Admittedly, as limited by the resolution of the SEM image, the SEM images are not able to illustrate how the nickel particles are dispersed in the alumina support. However, the EDX spectra for the spotted areas of the fresh catalyst surface prove the presence of Ni, Ru and Al as expected, and the EDX spectra for the spent catalyst evidence the char/coke deposition in an interesting form of spherical carbon particles.

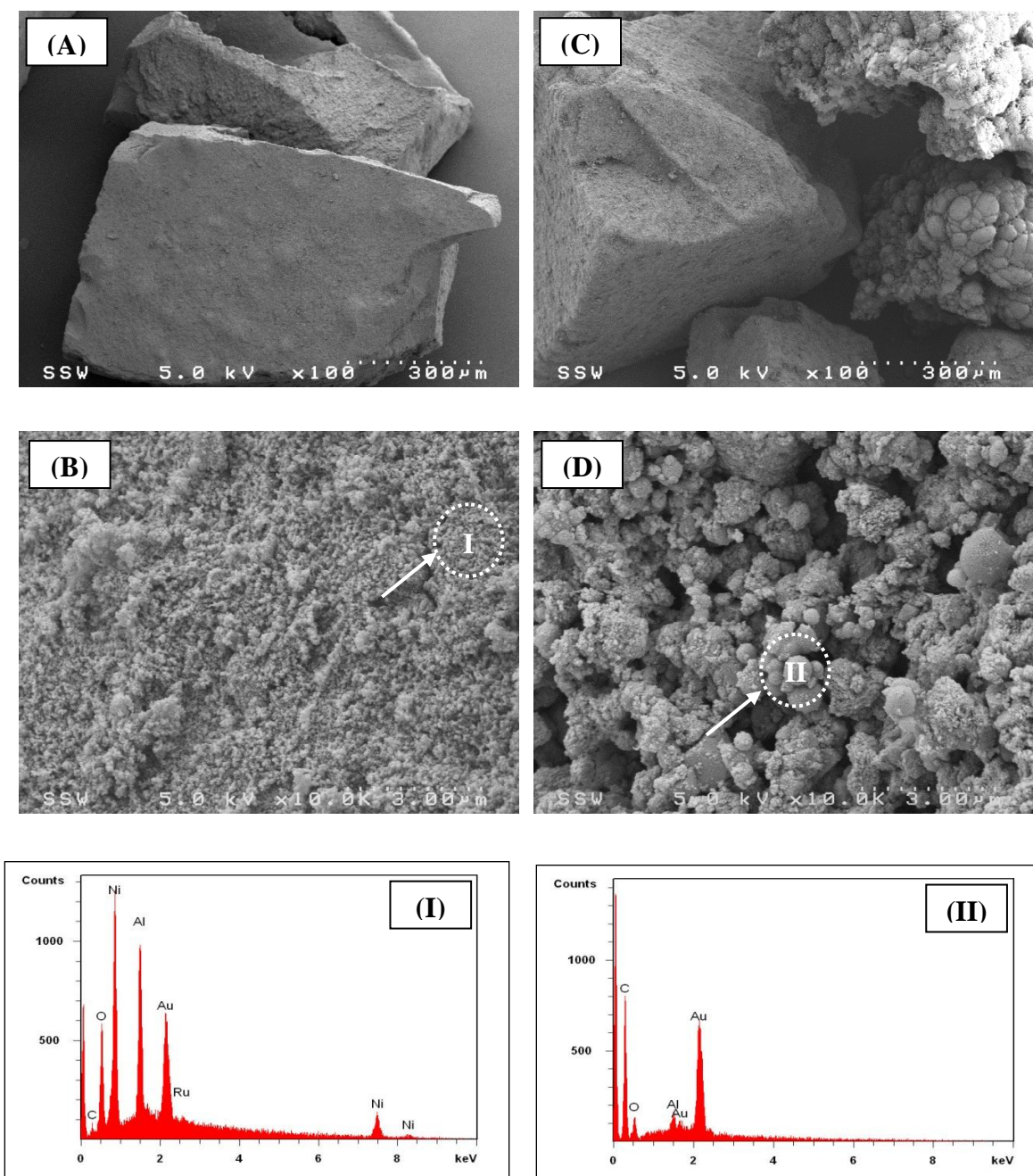


Figure 3.9 – SEM images for the fresh (not reduced) (A), (B) and used (after 20 hours experiment) (C) , (D) $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ catalyst, and EDX spectra for the spotted parts of the fresh (I) and used (II) catalyst.

In summary, the above catalyst characterizations results did evidence the formation and deposition of char/coke over the $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ catalyst during the SCWG experiments. As

shown previously, the catalyst remained its high activity after 20 hours, so the char formation and accumulation in the reactor did not appear to deactivate this catalyst.

3.4.4. Effects of nickel loading

The effect of nickel loading for the activity of γ -Al₂O₃ supported Ni-Ru catalysts (containing 2 wt.% ruthenium as a co-catalyst) has been shown briefly in the previous Figure 3.3, and is further discussed in this section. Using the impregnation method, 30 wt.% Ni, 20 wt.% Ni, and 10 wt.% Ni catalysts each with 2 wt.% Ru were loaded onto γ -Al₂O₃. The results of the gas yields with these three catalysts are comparatively presented in Figure 3.10. Increasing nickel loading from 10 to 20 wt.% increased the methane yield (accompanied by a significant decrease in H₂ yield) and resulted in a drastic increase in carbon gasification efficiency. It should be noted that nickel is a useful catalyst for catalyzing methanation reaction (Elliott et al., 1988, 1993; Sato et al., 2005; Sharma et al., 2006). Therefore, the direct correlation between nickel content and methane production may be expected. However, there is no significant change, rather a slight decrease in either methane yield or carbon gasification efficiency as the Ni loading increased further from 20 to 30 wt.%, which might be due to the deteriorated metal dispersion in the supported catalyst at a very high metal loading. This may be evidenced by the monotonically decrease in BET surface area and pore volume of the NiRu/ γ -Al₂O₃ catalysts when increasing the Ni loading from 10 wt.% to 30 wt.% (Table 3.1).

Additionally, an increase in Ni-loading consistently led to reduced yields of tar and char, and with Ni_{20%}Ru_{2%}/ γ -Al₂O₃ and Ni_{30%}Ru_{2%}/ γ -Al₂O₃ the tar formation was very low (<2 %), as summarized in Table 3.4.

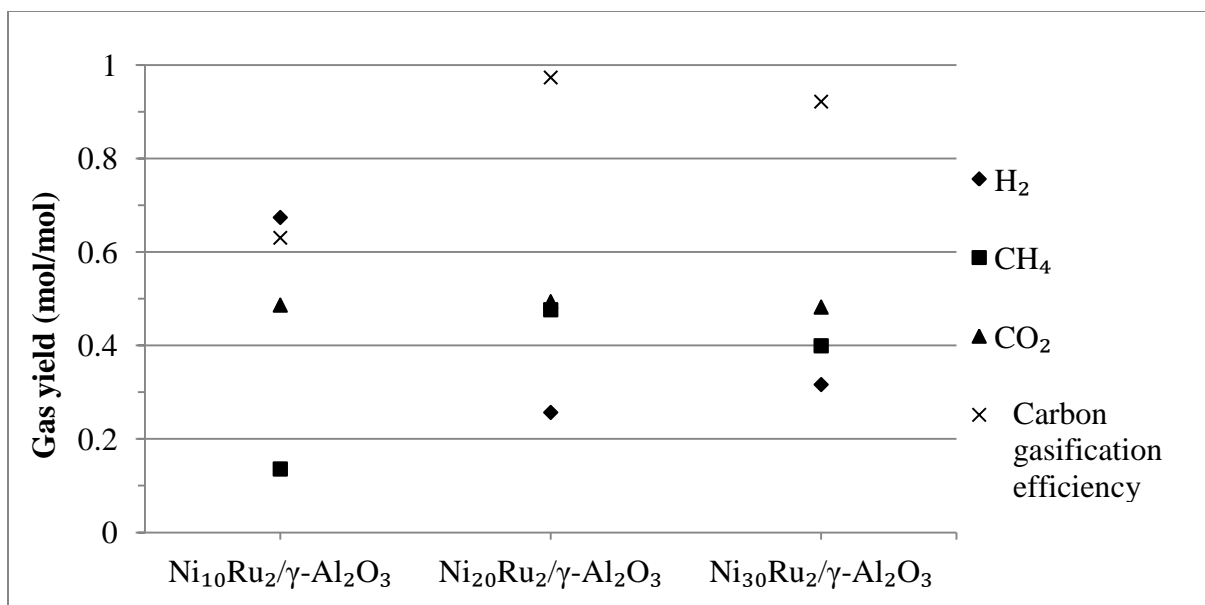


Figure 3.10 - Effects of different nickel metal loading on SCWG of 5 wt% glucose-water solution for 6 hour time on stream at 500 °C and 27.5 MPa.

3.4.5. Carbon balance

Overall results of all tests performed in this study are shown in Table 3.4. The detailed results were described and discussed in the previous sections. Total carbon distribution in terms of gas, liquid effluent, tar and char were analyzed to calculate the carbon balance for each experiment. The amount of carbon in the gas products was based on the GC analysis. Using TGA analysis, the amount of char/coke (assumed to consist of 100% C) was calculated based on the mass loss between 120 °C and 900 °C, which attributes to the combustion of char/coke and heavy organics that were deposited on the catalyst. The carbon distribution in the liquid effluent and tar were determined by TOC and elemental analysis (results are presented in Table 3.5). Thus, carbon balance for each experiment was calculated based on the weight percentage of recovered carbon in the gas (GC analysis), tar (elemental analysis), char (TGA analysis), and liquid effluent (TOC results). The carbon balance is shown in the Table 3.4. The carbon balance for all experiments falls in a reasonable range of 96-105 wt.%, suggesting acceptable accuracy of our experiments. The errors may come from various sources including: the analytical errors for various analytical instruments and the errors in collecting tar/char from the system.

Table 3.4 - Overall results of all tests performed in this study and carbon balance, T=500 °C, P=27.5 MPa, WHSV= 3 h⁻¹

Catalyst	WHSV (h ⁻¹)	Tar yield %	Char yeild %	Gas composition (vol%)					Carbon gasification efficiency (mol/mol)	Carbon balance (wt.%)
				CH ₄	H ₂	CO ₂	CO	C ₂ -C ₃		
Blank	NA	17.33	NA	1.5	40.5	41.5	14.7	1.8	0.12	101.3
Ni _{30%} Ru _{2%} /γ-Al ₂ O ₃	3	1.11	2.25	32.87	26.04	39.7	0	1.39	0.92	102.6
Ni _{20%} Ru _{2%} /γ-Al ₂ O ₃	3	1.66	2.11	38.8	20.89	40.2	0	0.11	0.98	98.7
Ni _{10%} Ru _{2%} /γ-Al ₂ O ₃	3	2.98	2.81	10.43	51.82	37.41	0	0.33	0.63	102.2
Ni _{20%} /γ-Al ₂ O ₃	3	3.11	1.92	8.16	44.8	46.7	0	0.34	0.71	98.8
Ru _{2%} /γ-Al ₂ O ₃	3	15	4.35	15.48	41.4	42.29	0	0.83	0.13	96
Ni _{20%} Ru _{2%} /TiO ₂	3	10.11	5.30	6.73	24.39	68.6	0	0.28	0.28	103.6

Table 3.5 - Elemental composition of tar collected from the experiments (500 °C, 6h on stream)

Test	C wt. %	H wt. %	O wt. %
Blank Test	69.23	6.17	24.6
Ni _{30%} Ru _{2%} /γ-Al ₂ O ₃	72.57	9.35	18.08
Ni _{20%} Ru _{2%} /γ-Al ₂ O ₃	66.45	8.09	25.46
Ni _{10%} Ru _{2%} /γ-Al ₂ O ₃	77.4	7.71	14.89
Ni _{30%} /γ-Al ₂ O ₃	75.89	8.16	15.95
Ru _{2%} /γ-Al ₂ O ₃	71.64	6.85	21.5
Ni _{30%} Ru _{2%} /TiO ₂	73.29	7.84	18.87

3.5. Conclusions

(1) Nickel and ruthenium metallic catalysts supported on γ-alumina, titanium (II) oxide, and activated carbon were screened with respect to carbon gasification efficiency, methane and hydrogen production yields from SCWG of glucose as a biomass model compound at 500 °C and 27.5 MPa in a down-flow tubular reactor. Ruthenium and nickel supported on γ-Al₂O₃ were found highly stable and active in the harsh conditions of SCWG of glucose.

(2) Only 0.13 mol/mole of carbon in the feedstock was converted into gases in the absence of any catalyst, and the rest remained in the liquid effluent or was converted into char and tar.

(3) The Ni_{10%}Ru_{2%}/γ-Al₂O₃ catalyst achieved the highest H₂ gas yield (0.68 mol/mol carbon-fed) in this study. However, this catalyst only converted 0.63 mol/mol of carbon in the feedstock into carbon-containing gaseous products, and produced much less methane (0.14 mol/mol carbon-fed) than Ni_{20%}Ru_{2%}/γ-Al₂O₃ (~0.5 mol CH₄/mol carbon-fed).

(4) The $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ catalyst demonstrated the highest gasification efficiency (>0.98 mol/mol) and activity towards methane production, with 0.5 mol CH_4 /mole of carbon in feedstock.

(5) Ruthenium proved to be an excellent promoter or co-catalyst to nickel catalyst for SCWG of biomass. Addition of ruthenium metal to Ni catalysts promoted the catalyst activity and suppressed char/tar formation. The promoter roles of Ru in the Ni-catalysts include increasing nickel metal dispersion on the support, improving nickel reducibility, preventing reactor plugging due to char/tar suppression.

(5) Experiments for an extended duration of time (20 h) demonstrated that the $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ catalyst retained its high activity for carbon gasification and methanation efficiency for up to 20 h on-stream without any indication of reactor plugging and catalyst deactivation.

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CHAPTER 4. SUPERCRITICAL WATER GASIFICATION OF AQUEOUS FRACTION OF PYROLYSIS OIL IN THE PRESENCE OF A NI-RU CATALYST

4.1. Introduction

Depletion of fossil fuels, environmental issues concerning them and also global warming as a consequence of CO₂ emissions have pressed scientists to find renewable and widely available substitutes. Biomass energy is abundant, clean, and carbon neutral, so it has great potential in substituting fossil fuels for both energy and chemicals. This energy can be transferred into heat and electricity by direct combustion of the biomass, or converted into liquid/gaseous fuels through various thermochemical and biochemical processes. Thermochemical approaches include hydrothermal processes such as hydrothermal liquefaction (HTL) and supercritical water gasification (SCWG). SCWG is very promising for converting high water content biomass or waste water slurries (even > 90%) into green fuels. Hydrogen is a valuable gas which is commercially produced from the reforming of natural gas widely used for the growing fuel cell market and in large amount for ammonia synthesis. On the other hand, synthetic natural gas (SNG) is considered as another probable energy carrier when it is derived from biomass. Moreover, Bio-SNG meets all regulations including the EU Regulation for CO₂ emissions.

Among the thermochemical processes, supercritical water gasification (SCWG) of biomass is a viable option for the production of bio-SNG and syngas. Water above its critical point, 374 °C and 22.1 MPa, is called supercritical water, which has superior solubility of organic compounds and poor solubility of inorganics (Savage, 1999). As an innovative thermo-chemical approach, this highly pressurized water environment has received lots of attention during the past three decades with the pioneering work by Modell at MIT (1982; Lu et al., 2012). In contrast with other hydrothermal processes, SCWG of biomass does not require feedstock drying, even for water contents > 90%. Depending on the operating conditions and type of catalyst, the product gas composition can be directed to produce methane or hydrogen rich gas, with typical gas products including methane, hydrogen, carbon dioxide, carbon monoxide, water vapor, and low concentrations of C₂-C₃ gases.

Fast or flash pyrolysis, operating at relatively low temperatures of typically 500 – 650 °C with high heating rates of 1000 °C/s (or even 10000 °C/s), is so far the only technology demonstrated to be practical/commercially feasible on a large scale for the production of bio-oils from biomass. This convert's dry biomass by condensing the vapors produced and rapidly heating in the absence of oxygen, providing a liquid product termed bio-oil or pyrolysis oil. Fast pyrolysis offers an economically viable solution to densification of the bulky biomass feedstock into an energy intermediate product (bio-oil) with a significantly improved volumetric energy density. Bio-oil from fast pyrolysis however has high contents of oxygen (35-40 wt.%) and water (up to 50 wt.%), resulting in relatively low gross heating values (normally <20 MJ/kg, only about half of that of petroleum). The bio-oil could be easily steam reformed (Ramachandran et al., 2009, 2011) to produce synthesis gas (syn-gas), which can be further be upgraded by Fisher–Tropsch synthesis into liquid fuels.

Water-containing pyrolysis oil can be upgraded to improve its heating value by removing its water fraction. The water fraction from pyrolysis oils generally contains mainly water, carbohydrates, phenolic compounds, acetic acids, and other organic compounds (Vispute and Huber, 2009). Hydro-de-oxygenation (HDO) is another viable option for bio-oil upgrading to decrease the oxygen content and increase the H/C ratio of the oil. The hydro-treated bio-oils give much higher heating values which can then be used as a combustion fuel. In addition, their better compatibility with hydrocarbons allows them to be mixed with petroleum feeds for co-processing in existing petro-refineries (Miguel et al., 2011). However, the HDO process generates a high yield (up to 70 wt.%) of aqueous by-products. Similar to the water fraction separated from pyrolysis oil, these by-products contain mainly water and lots of organic compounds such as, carbohydrates, phenolic compounds, and acetic acids, etc. These aqueous by-product streams and the aqueous fraction from pyrolysis oil containing high TOC value must then be treated before discharging to the municipal wastewater facilities. Treatment of the aqueous by-product streams could help reduce its TOC value, enabling energy recovery in the form of methane and hydrogen fuel gases, being a driving force for this research.

Several researchers have studied SCWG of real aqueous biomass such as the water soluble fraction of pyrolysis oil (Chakinala et al., 2012), wood (Waldner and Vogel, 2005), wood sawdust (also rice straw, rice shell, wheat stalk, peanut shell, corn stalk, corn cob and sorghum

stalk) (Lu et al., 2006) and waste streams generated from a sludge hydrothermal liquefaction process (Zhang et al., 2011). A sludge from a hydrothermal liquefaction process was successfully converted into gaseous products with 48.5 vol % hydrogen and 14.6 vol.% methane at 750 °C and 24 MPa, and 96.6 % carbon gasification efficiency were obtained in presence of 0.1RuNi/ γ -Al₂O₃ catalyst (Zhang et al., 2011). 13.5 mol H₂/kg sludge (on a dry basis) from the SCWG of 2.8 wt.% sewage sludge in a flow reactor at 600 °C and 34.5 MPa in the presence of a coconut shell activated carbon catalyst (Xu et al., 1996). Although some groups have demonstrated successful results with real biomass, there is not much research on the SCWG of water soluble products from pyrolysis oil.

To obtain bio-fuels biomass including wood or algae (Chakinala et al., 2009; Waldner and Vogel, 2005), several researchers have studied the method of using catalytic gasification in supercritical water of the water-soluble fraction of bio-oil. The most commonly used heterogeneous catalysts were alumina-supported Pt, Pd, Ru, Rh, and Ni (Chakinala et al., 2012). However, during continuous operation at 400 °C and 300 bar using wood liquefaction products as a feed, Raney nickel was reported to exhibit high initial activity but sintered rapidly, accompanied with a loss of metal surface area. The most significant problem in the SCWG process is to modify the catalyst for suitable operation in hydrothermal gasification at reasonable operating conditions.

In the first part of this chapter, a glucose-water solution was used as a model to explore the temperature and WHSV effects on SCWG efficiency. Then, the Ni_{20%}Ru_{2%}/ γ -Al₂O₃ catalyst, which was determined to be the most effective catalyst in last chapter will be investigated for methane and hydrogen production from the aqueous fraction of pyrolysis oil. Since the aqueous phase contains a variety of carbon contained matters, the SCWG of this fraction of pyrolysis oil will be compared with the model compound glucose.

4.2. Materials and methods

4.2.1. Feedstock and Catalyst preparation:

A batch solution of 50 g/L glucose-water was prepared by dissolving α -D-glucose (Sigma Aldrich) in distilled water. The biomass used in the subsequent part of this study was the aqueous fraction of pyrolysis oil from hardwood sawdust at ICFAR institution conducted by

colleagues at ICFAR, Western University, Canada. The water soluble part of the oil comprised 13 wt.% carbon and 71 wt.% water. The water content was determined by Karl Fisher titrations (titrant: combi Titrant 5, CombiSolvent keto, Mettler Toledo KFTitrator). The aqueous pyrolysis oil fraction was filtered (1 μm), centrifuged, and left overnight to precipitate any oil remaining in the water phase. The real aqueous biomass feed was prepared from this 13 wt.% C and diluted to five (DA5) and twenty times (DA20). The TOC analysis showed 0.7 and 2.98 wt% carbon content for DA5 and DA20, respectively. To prevent or slow down the re-polymerization of compounds inside the aqueous fraction of pyrolysis oil (which would precipitate out), it was diluted five and twenty times.

The nickel-ruthenium catalyst was prepared by the co-impregnation of the metal salts (Lee and Ihm, 2008) onto a γ -alumina support in the form of nickel (II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), and ruthenium (III) nitrosyl nitrate solution in dilute nitric acid ($\text{HN}_4\text{O}_{10}\text{Ru}$) from Sigma-Aldrich. The metal support was $\gamma\text{-Al}_2\text{O}_3$ from Inframat Advance Materials with a BET surface area of 154.1 m^2/g . After impregnation the catalyst was oven dried for 16 hours at 110° C. The dried material was calcined in air at 600 °C (10 °C/min heating rate) for 6 hours. After cooling, the catalyst material was crushed and sieved to a nominal average diameter of 575 μm (mesh size 300-850 μm , ACS). The BET surface area for this catalyst was measured as 126.5 m^2/gr .

4.2.2. Apparatus and experimental procedure

A continuous-flow tubular reactor constructed from Inconel 625 tubing with dimensions of 9.55mm OD×6.34mm ID×472 mm length was used in this study. The tube was heated in an electrical furnace. A porous stainless steel filter (mesh size 80) was used to support the catalyst particles inside the tubular reactor. A small amount of quartz wool (1 cm depth) was placed before the support to minimize any catalyst loss by entrainment. Feedstocks were pumped by an HPLC pump (Eldex, optos series) to the top of system to provide a down-flow regime inside the reactor. The feedstock was fed at 1 mL/min which translates to a WHSV (weight hourly space velocity, the flow-rate of reactant per mass of the catalyst) of 3 h^{-1} , unless stated otherwise. Reactor pressure was maintained at a constant 4000 psi (~27.5 MPa) by a back-pressure. Due to laboratory limitations, experiments were only carried out for 6 hours. A schematic diagram of the supercritical water gasification reactor was provided in the last chapter.

4.2.3. Gas and liquid product analysis

Gas products were collected in a gas bag (1 L) about almost every hour, and a known volume of nitrogen gas was injected the bag as an internal standard by a sensitive syringe from SGE Analytical Science (500 mL). The gas samples were analyzed with a micro-GC (Agilent 3000A, Cerity software) equipped with dual columns (Molecular weight and PLOT-Q) and thermal conductivity detectors (TCD). Liquid effluents were also collected in parallel to gas samples and analyzed for TOC using a Shimadzu TOC-V CPH instrument. Catalyst stability testing was verified by inductively coupled plasma-atomic emission spectrometry (ICP-AES) from PerkinElmer (Optima 3000) analysis to trace any metals in case any leaching has happened.

4.2.4. Tar and char analysis

After each experiment, the reactor was cooled down to room temperature by removing the heat source and injecting cold water into the system. Then A.C.S. reagent-grade ethyl acetate solvent was pumped into the system to collect any water insoluble organic residues in the interior of the reactor and the catalyst bed. This water-solvent solution was separated by a liquid-liquid decanter, and the solvent phase was evaporated by a rotary evaporation at 60 °C under reduced pressure to evaporate the solvent. The remaining viscous liquid was referred to as tar, which is a undesired product of the SCWG process (Calzavara et al., 2005). Elemental analyzer Flash EA 1112series CHNS-O was utilized to determine the composition of the tarry samples. The spent catalyst was removed from the tubular reactor and characterized by thermogravimetric analysis (TGA) (SDT Q600 from TA Instruments) to evaluate the amount of carbon/coke deposits on the catalyst after each experiment. The spent catalyst samples were heated up to 900 °C under a 40 mL/min air flow rate at ambient air pressure with a 10 °C/min heating rate. The weight loss between 120 °C and 900 °C may be attributed to carbon/coke deposition on the catalyst. Scanning Electron Microscopy coupled with Energy Dispersive X-ray (SEM/EDX), Physical Electronics Model PHI 660, also used which displays the deposition of carbon base residues on the catalyst.

4.3. Definitions

To explore the efficiency of the catalyst for converting carbon containing feedstocks into gaseous products, the following terms are defined. Yields are defined based on the moles of gas in the products per mole of carbon in the feedstock fed to the reactor.

$$\text{Hydrogen production yield (mol/mol)} = \frac{\text{Moles of H}_2 \text{ recovered in gas}}{\text{Total moles of carbon fed}} \quad (\text{Eq. 4.1})$$

Carbon gasification efficiency defines how much carbon from feedstock is been converted into carbon-containing gaseous products, which are mainly CH₄, CO₂, and CO. Other carbon containing gases are very negligible in the produced gas.

$$\text{Carbon gasification efficiency (mol/mol)} = \frac{\text{Moles of carbon recovered in gas}}{\text{Total moles of carbon fed}} \quad (\text{Eq. 4.2})$$

For char and tar production, other terms are defined as follows:

$$\text{Tar yield (wt.\%)} = \frac{\text{Total mass of carbon from tar recovery}}{\text{Total mass of carbon fed}} \times 100\% \quad (\text{Eq. 4.3})$$

$$\text{Char yield (wt.\%)} = \frac{\text{Total mass of char recovered}}{\text{Total mass of carbon fed}} \times 100\% \quad (\text{Eq. 4.4})$$

4.3.1. Effects of temperature and WHSV on the gasification of glucose

In the last chapter, it was found that the Ni_{20%}Ru_{2%}/γ-Al₂O₃ catalyst was the most effective in terms of carbon gasification efficiency for SCWG of 5 wt.% glucose-water solution at 500 °C. Gasification temperatures from 400-600 °C were examined with the WHSV, pressure, and catalyst bed kept constant for all experiments, as shown in Figure 4.1. As can be seen in this figure, higher temperatures result in higher gas yields, and the carbon gasification efficiency is approximately 1 mol/mol at or above 500 °C. This suggests that almost all the total carbon in the glucose-water solution is already converted to gaseous products at 500 °C. Based on thermodynamic equilibrium calculations (Figure 2.1 in previous chapter 2), hydrogen production

is increased at higher temperatures. The results show that hydrogen production is increased with temperature, which affects the water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$) (Guo et al., 2010). Carbon dioxide production is also enhanced at higher temperatures, as shown in Figure 4.1. Carbon gasification efficiency and all gas yields are low at 400 °C, which increase with temperature. Methane production increases from 400 to 500 °C, but it maximizes at 500 °C, and decreases from 500 to 600 °C, which is also expected from the thermodynamic equilibrium, but the lowest amount of this gaseous product can be seen at 400 °C. This may be because of kinetically poor conditions at 400 °C which is not a favorable temperature for methanation or the water-gas shift reaction, and generates mostly CO_2 through steam reforming reactions.

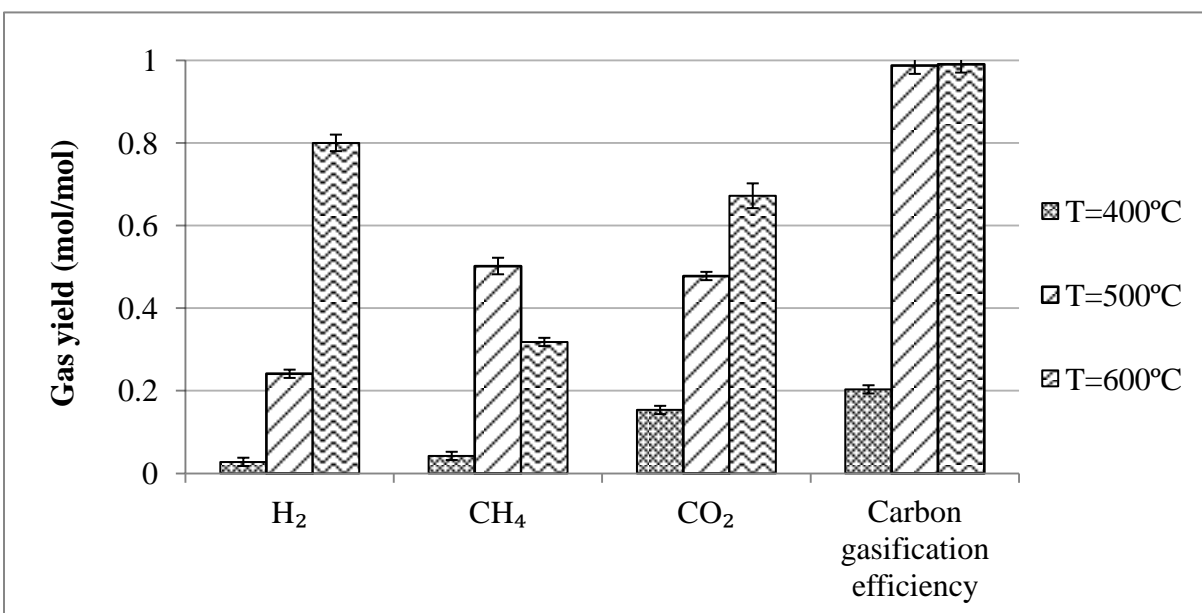
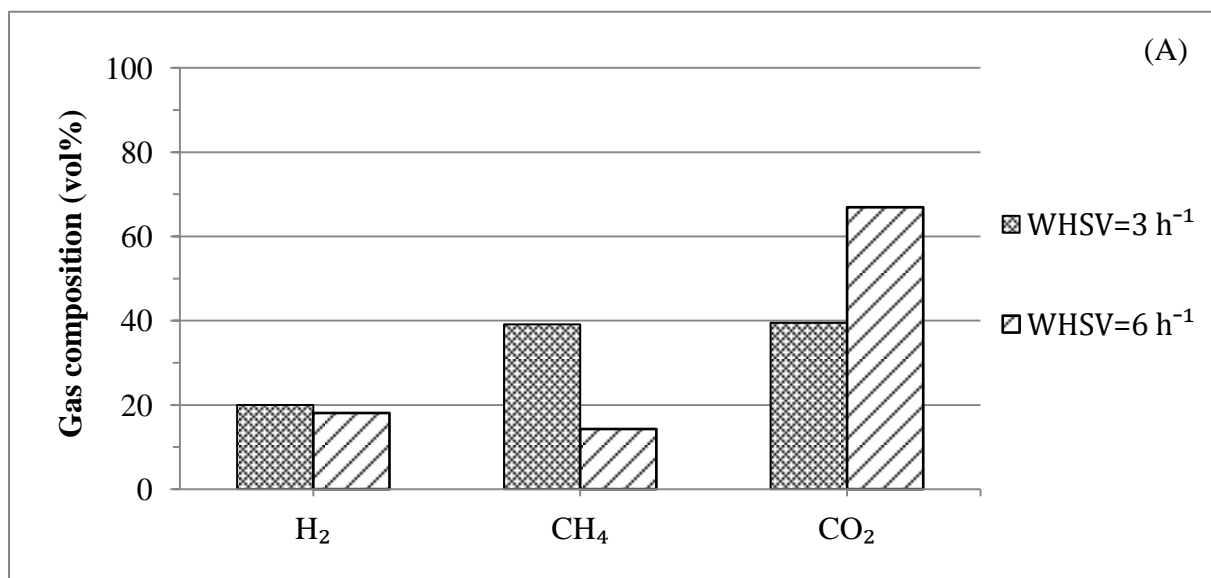


Figure 4.1 - Gas yields from SCWG of 5 wt% glucose-water solution at 400-600 °C. P=27.5 MPa, WHSV=3 h⁻¹

In addition to temperature, the amount of catalyst and the feeding rate of the feedstock both affect the selectivity and activity of the catalyst. The WHSV covers both these effects in one unit term, defined by the flow rate of reactant per amount of catalyst. There are two ways to change the WHSV parameter: 1- changing the flow-rate and keeping the catalyst amount constant. In other words, increasing the flow-rate, for instance, to double of it means that the WHSV increases to double as well. 2- keeping the flow-rate constant but changing the catalyst amount. For example, if one reduces the catalyst amount to half, the WHSV doubles. In this study, the

second method was used as preliminary tests show that increasing the feeding rate with the same amount of catalyst led to possible plugging of the reactor. In this study, WHSV=6 h⁻¹ was examined and compared with 3 h⁻¹ (other parameters kept constant). The results are shown in Figure 4.2. It can be seen from the figure that at WHSV of 6h⁻¹, all gas yields are much lower than that at WHSV of 3 h⁻¹. For higher gasification efficiencies, higher temperature or longer residence times are required (Lu et al., 2006). It has been demonstrated that longer residence time at low temperatures results in high methane production, and high temperatures at low residence time will favor hydrogen production (Byrd et al., 2007). Methane concentration drastically decreases from 39 vol% at WHSV of 3 h⁻¹ to 14 vol% at WHSV of 6 h⁻¹, and Carbon dioxide increases from 40 to 67 vol%.

High feeding rates at the initial stages of the experiment may generate higher amounts of tar and char. This initial tar produced is hard to be gasified (Chuntanapum and Matsumura, 2010), and may cause reactor plugging. Therefore, lower amounts of catalyst were chosen to prevent this phenomenon in this study.



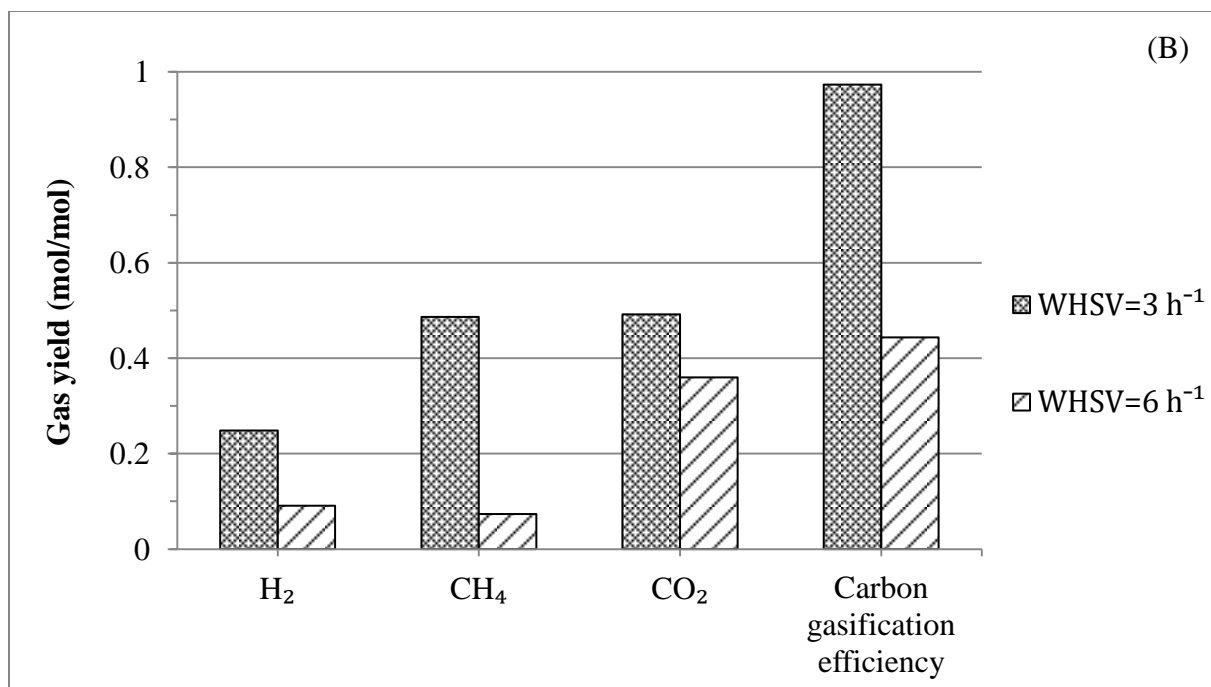


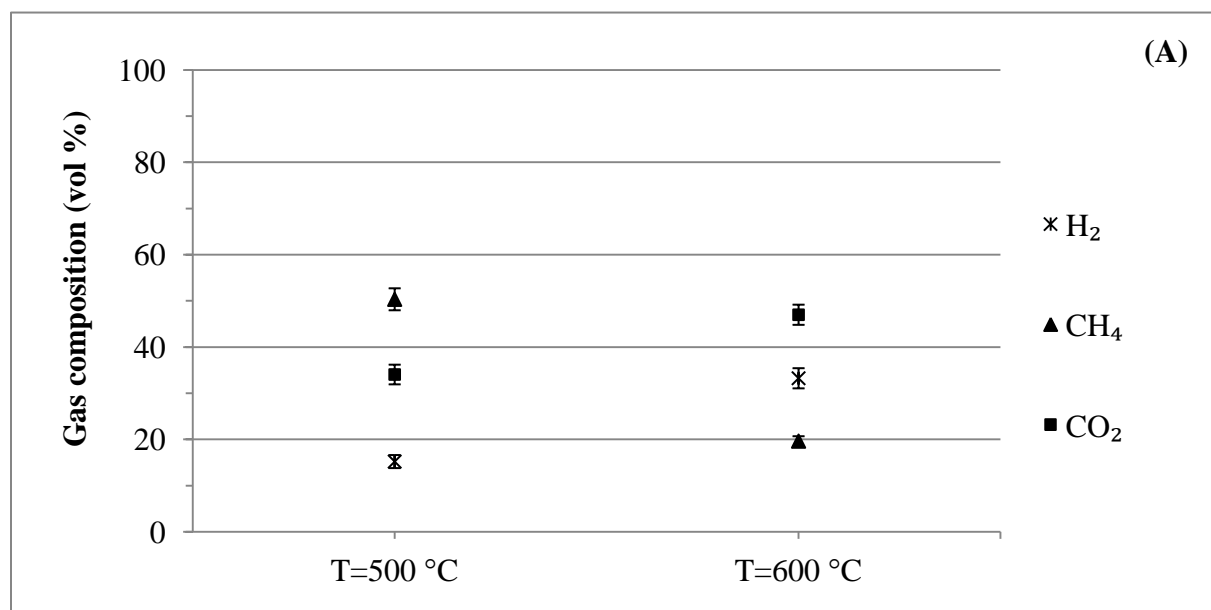
Figure 4.2 - Effect of WHSV on gas yields (A) and composition (B) from SCWG of 5 wt.% glucose-water solution at T=500 °C and P=27.5 MPa in presence of Ni_{20%}Ru_{2%}/γ-Al₂O₃.

Since the reaction kinetics are slow at lower temperatures (such as examined in this study), high residence times are needed to reach equilibrium (Voll et al., 2009). In other words, the catalyst should be in contact with the feedstock for sufficient time to be able to complete the gasification reactions. Figure 4.2 shows that higher examined WHSV value (or a shorter residence time) results in a weaker carbon gasification efficiency and lower gas production. With the catalyst at WHSV=3 h⁻¹, higher amounts of methane were produced in comparison with WHSV=6 h⁻¹ in SCWG of the glucose-water solution. This result is consistent with the literature where methane production was found more favorable at lower temperatures and higher residence times (Mozaffarian et al., 2004).

4.3.2. Effects of temperature on SCWG of aqueous phase of pyrolysis oil

Aqueous biomass investigated in this work was the water-soluble phase of pyrolysis bio-oil. The SCWG of DA20 was carried out at 500 – 600 °C, 27.5 MPa, and WHSV of 3 h⁻¹ in the presence of Ni_{20%}Ru_{2%}/γ-Al₂O₃ catalyst. The results are summarized in the Figure 4.3 (A) and (B). A high fraction of the carbon from the aqueous biomass was converted into gaseous products. At 600 °C,

0.91 mol/mol carbon gasification efficiency shows the high potential of this Ni-Ru catalyst. The hydrogen yield increases drastically from only 0.13 mol/mol at 500 °C to 0.45 mol/mol at 600 °C. Therefore, higher temperatures are necessary to obtain a hydrogen rich gas. Since almost complete carbon conversion efficiency (0.91 mol/mol) was achieved at 600 °C, higher temperatures were not examined. However, a higher temperature SCWG test will be discussed later in this section for feedstock of higher carbon content. In the model compound test using glucose, it was also observed that from 500 – 600 °C, methane production decreased while hydrogen production increased. Although, high amounts of hydrogen were produced from SCWG of glucose i.e., 0.8 mol of H₂/mole of C in the feedstock, the SCWG of real aqueous biomass at 600 °C gave only 0.45 mol H₂/mol of C in feedstock. This may be due to the lower amount of hydrogen content in the DA20 feedstock. To demonstrate the accuracy of the test, error bars based on the average of two trials for each experiment are expressed in the following graphs.



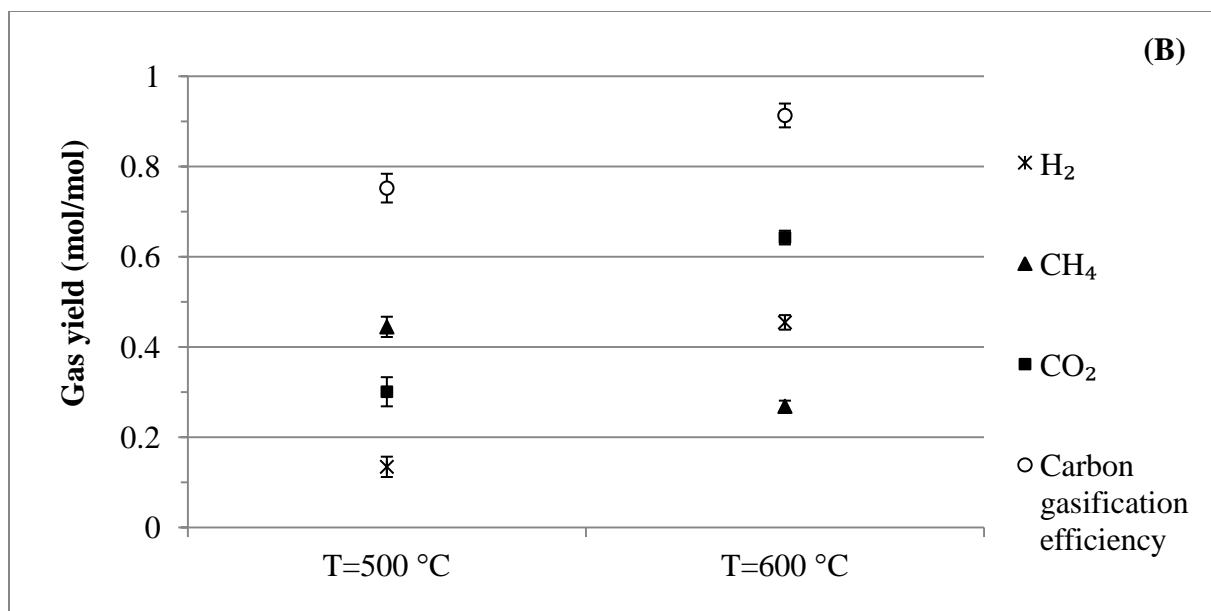


Figure 4.3 - Temperature effect on gas composition (A) and gas yields (B) from SCWG of DA20 at T=500-600 °C, P= 27.5 MPa, WHSV=3 h⁻¹ in presence of Ni_{20%}Ru_{2%}/γ-Al₂O₃.

These experiments were repeated with a more concentrated solution of the pyrolysis oil aqueous phase (2.98 wt.% C). The results of these experiments are presented in Figure 4.4. Very low carbon gasification efficiency was achieved at 600 °C and most of carbon in the feedstock was converted into liquid products and char. High carbon content and complex structure of this aqueous biomass makes it hard to predict possible reasons for this low carbon gasification efficiency. Hydrolysis of biomass generates low molecular weight fragments which may be reactive functional compounds. Then a cross-linking between these components and biomass residue yields higher molecular weight fragments which may be harder to gasify (Saisu et al., 2003). Therefore, a successful SCWG highly depends on the nature of biomass (Yoshida et al., 2004). Most of the carbon from SCWG of DA5 at 600 °C converted into the liquid effluent with a small amount of char production. However, increasing the reaction temperature to 700 °C led to the production of 1.18 mol H₂/mol of carbon in feedstock and almost complete carbon gasification efficiency.

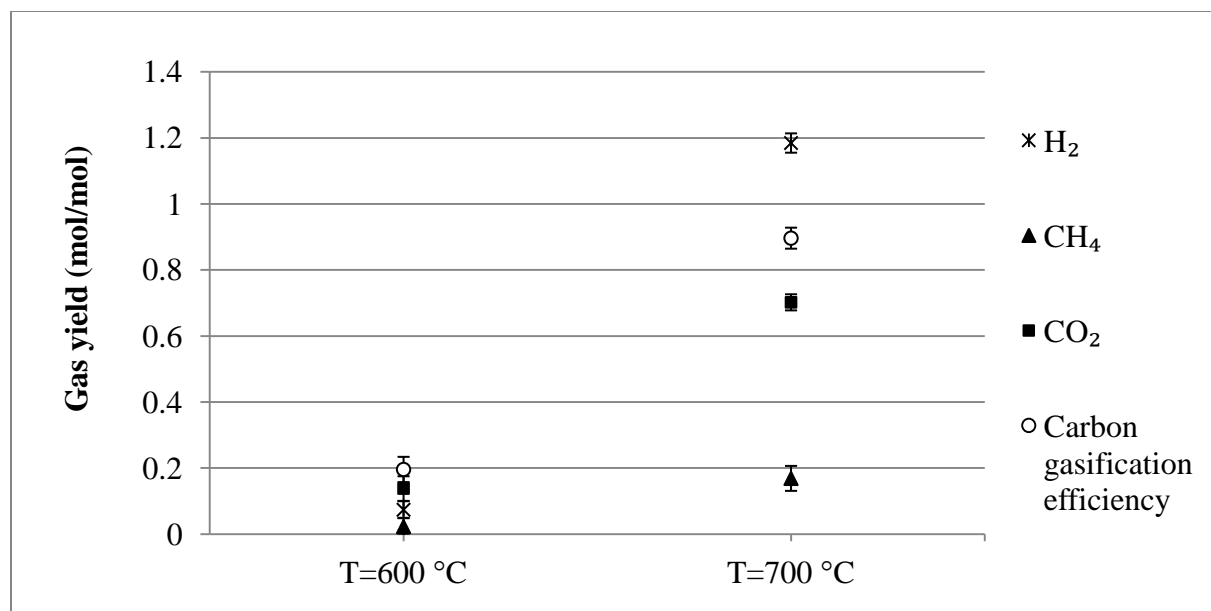


Figure 4.4 - Temperature effect on gas yields from SCWG of DA5 at T=600-700 °C, P= 27.5 MPa, WHSV=3 h⁻¹ in presence of Ni_{20%}Ru_{2%}/γ-Al₂O₃.

Comparing these results with the SCWG of DA5 at 700 °C in the absence of any catalyst (blank test), as shown later in Table 4.2, the necessity of a catalyst is clearly indicated. Only 0.68 mol C /mol-C-fed was obtained into gaseous products in the blank test without catalyst. In the presence of Ni_{20%}Ru_{2%}/γ-Al₂O₃, the carbon conversion increased to 0.89 mol/mol-C-fed and hydrogen production was drastically increased from 0.55 to 1.18 mol/mol of C in the feedstock. This comparison implies that the high temperature SCWG process can be a solution for high carbon content aqueous biomass in the presence of Ni-Ru catalyst. Hydrogen may also be the main component which can be used for fuel cells.

4.3.3. Effects of feedstock concentration

To explore the effects of feedstock concentration, results from the SCWG of DA5 and DA20 at 600 °C are comparatively illustrated in Figure 4.5. It can be seen that substrate concentration plays a very important role. The carbon gasification efficiency drops from 0.91 mol/mol to only 0.2 mol/mol-C-fed when the feedstock concentration was increased from 7 g/L to 30 g/L. No significant amount of tar production was observed using either DA5 or DA20 feed, and the high TOC content of the liquid effluent shows most of the carbon was retained in the liquid phase. This lower activity might be due to deactivation by char/coke deposition or catalyst pore

blocking by polymerization of furfurals, phenolic compounds, or other materials forming tar and char deposition. Hydrolysis of sugar compounds to smaller sugar units is followed by decomposition and depolymerization reactions to short-chain aldehydes and organic acids, which will compete with dehydration and ring-closure reactions to furfurals and phenols (Kruse et al., 2003). Although, both groups will react to desirable gas products, decomposition of phenols and furfurals are more slowly. It may leads to char/tar production or may temporarily mask the active surface of catalyst and lower the efficiency.

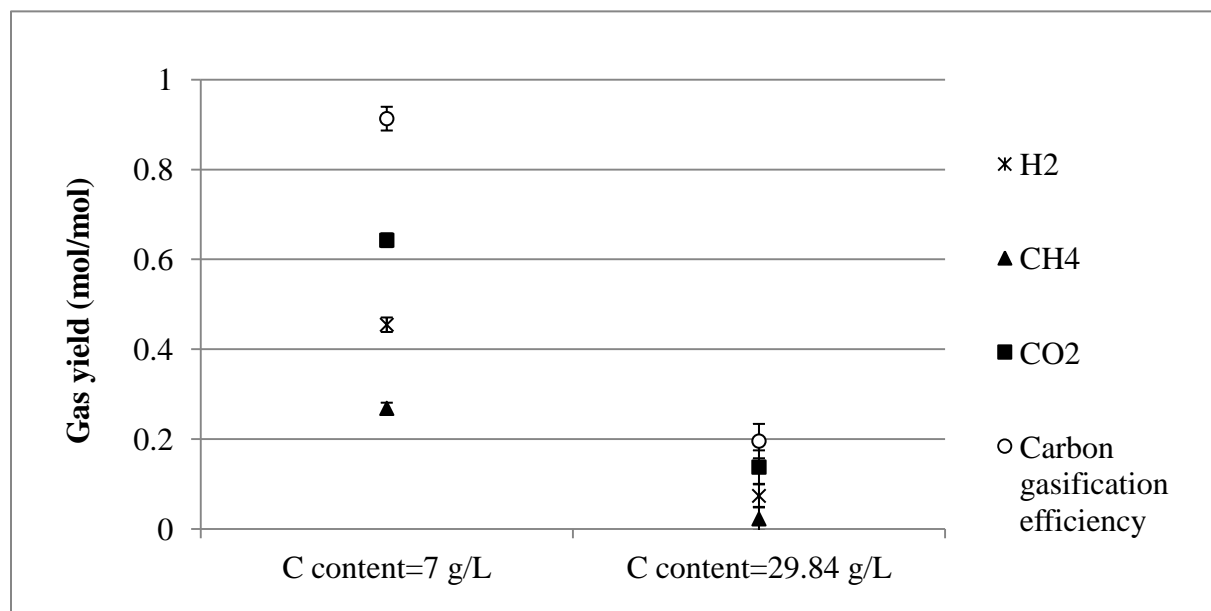


Figure 4.5 - Concentration effect on gas yields from SCWG of DA5 and DA20 at T=600 °C, P= 27.5 MPa, WHSV=3 h⁻¹ in the presence of Ni_{20%}Ru_{2%}/γ-Al₂O₃.

4.3.4. Catalyst Characterization

Figure 4.6 displays the SEM images of the spent Ni_{20%}Ru_{2%}/γ-Al₂O₃ catalyst after SCWG of the more concentrated feed (DA5) at 700 °C. It can be seen that the catalyst was contaminated by carbon deposition from 6 hour SCWG experiment. Figure 4.6 (C) and (D), show the areas of catalyst used for the subsequent EDX analysis as shown in Figure 4.7.

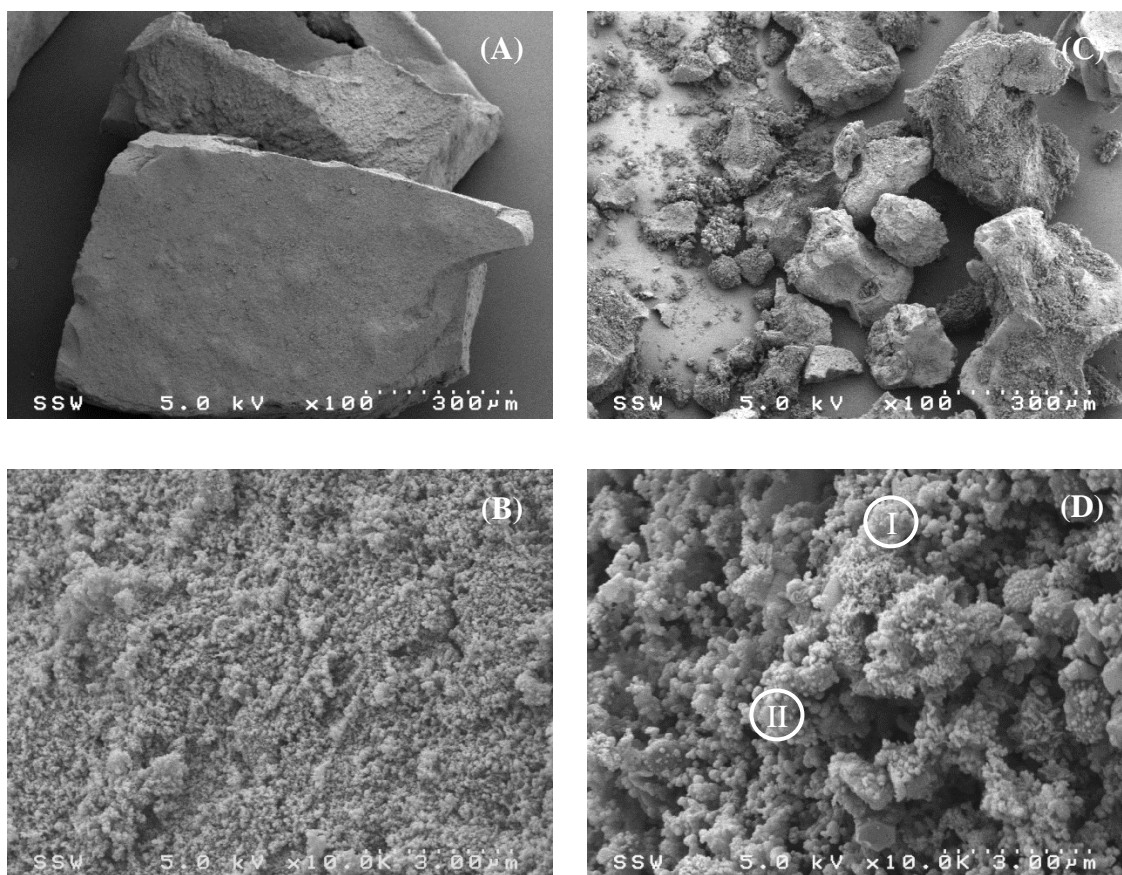


Figure 4.6 - SEM analysis of fresh (A), (B) and used (C), (D) $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ after 6 hours SCWG of DA5 at $T=700\text{ }^\circ\text{C}$, $P=27.5\text{ MPa}$, $\text{WHSV}=3\text{ h}^{-1}$.

The spherical particles on the surface of the spent catalyst are attributed to char/coke particle formation. Comparing micrographs (B) and (D) shows the different morphologies of the fresh and spent catalyst. This char production may lead to lower activity and lifetime of the catalyst.

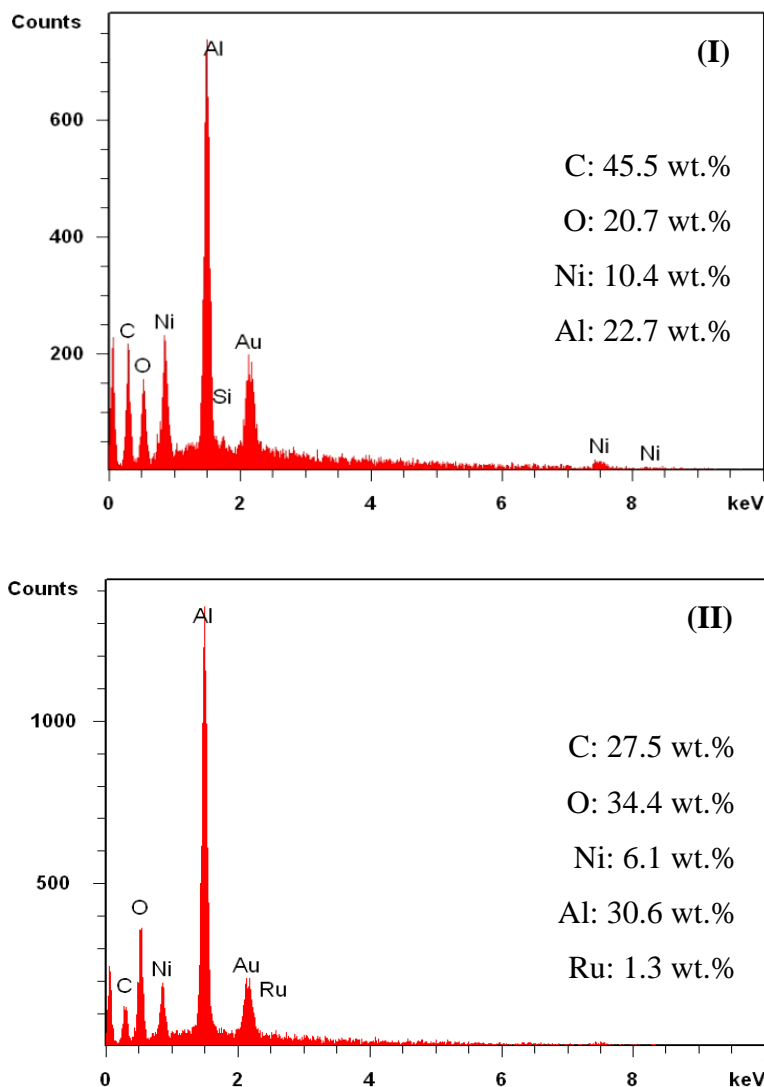


Figure 4.7 - EDX analysis for the used $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ catalyst after 6 hours SCWG of DA5 at 600 °C at two points of (I) and (II).

Although the EDX method cannot give a precise loading of metal on the catalyst surface, these figures for the used catalyst show the existence of considerable amount of carbon deposits.

Table 4.1 lists ICP results from DA5 and DA20 feedstock and from liquid effluent after 6 hours SCWG of different temperature ($P= 27.5 \text{ MPa}$, $\text{WHSV}=3 \text{ h}^{-1}$, in the presence of $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ catalyst). It should be noted, some metals (such as Na, K, Fe, Si, Ca, Al) may also exist in the pyrolysis oil and hence the aqueous fraction which may come from the original biomass ash component. It should also be noted that no Ru was reported in this Table as the ICP equipment

was not calibrated for the lack of suitable Ru standard solutions. The ICP analysis results for the liquid effluent and the feedstock as displayed in Table 4.1 do evidence the possibility of metal leaching during the experiments (Table 4.1). The Ni concentration in the effluent is significantly higher in the liquid effluent than that in the feedstock, except for the effluent with DA5 at T=600 °C (perhaps due to the analytical errors). There is no much difference in Al concentration between the feedstock and the effluent, suggesting that γ -Al₂O₃ support is stable under the SCWG conditions. A longer reaction time may lead to leaching of the metal catalyst to a larger extent, which might consequently deactivate the catalysts. As such, seeking catalyst with better resistance to metal leaching would be a focus of the future work.

**4.1 - ICP results from DA5 and DA20 feedstock and from liquid effluent after 6 hours
SCWG of different temperature (P= 27.5 MPa, WHSV=3 h⁻¹, in the presence of
Ni_{20%}Ru_{2%}/γ-Al₂O₃ catalyst)**

Element (g/L)	ICP analysis				
	Feedstocks		Liquid Products		
	DA5 0.7 wt.% C	DA20 2.98 wt.% C	DA5 at T=700 °C	DA20 at T=600 °C	DA20 at T=500 °C
Ni	0.0002	0.0001	0.004	0.008	0.01
Ru	0	0	0	0	0
Al	0.025	0.012	0.003	0.003	0.001
Ca	.012	0.007	0.280	0.291	0.29
Cu	0	0	0	0.0009	0.001
Fe	0.019	0.005	0.0002	0.001	0.004
K	0.030	0.021	0.03	0.028	0.028
Mg	0.003	0.002	0.086	0.089	0.09
Na	.324	0.026	0.511	0.55	0.556
Si	0.076	0.065	0.123	0.178	0.389

All the experimental results from SCWG of the pyrolysis bio-oil aqueous fraction are summarized in Table 4.2, where the carbon deposition on the catalyst was determined by TGA. As shown in the table, the reaction temperature and substrate concentration both significantly affect the carbon deposition. Carbon deposition decreased with increasing the reaction temperatures during the SCWG of either DA20 or DA5, but more carbon deposition was observed with the more concentrated feedstock (i.e., DA5) than DA20 at 600 °C. No tar was observed in the presence of catalyst almost in all experiments except for the SCWG of DA20 at a low temperature (500 °C). The absence of the catalyst resulted in significant amount of tar production (6.5 wt.%). These results illustrate the activity of the Ni-Ru catalyst for SCWG of aqueous fraction of pyrolysis oils, while suppressing tar production.

4.2 - Summary of SCWG of aqueous fraction of pyrolysis oil with different concentrations at 500-700 °C in presence of Ni₂₀%Ru₂%/γ-Al₂O₃ catalyst after 6 hours.

Feedstock	Feedstock C concentration (wt.%)	T (°C)	Tar yield (%)	Carbon deposition (%)	Gas yields (mol/mol of C in the feedstock)				Carbon converted into the gas (mol/mol)
					CH ₄	H ₂	CO ₂	CO	
DA5 (Blank test)	2.98	700	6.50	na ^a	0.11 ± 0.01	0.55 ± 0.02	0.53 ± 0.02	0.03	0.68 ± 0.01
DA5	2.98	700	nd ^b	2.14	0.17 ± 0.01	1.18 ± 0.03	0.7 ± 0.02	0.02	0.89 ± 0.02
DA5	2.98	600	nd	2.33	0.03 ± 0.01	0.07 ± 0.02	0.14 ± 0.03	0	0.19 ± 0.03
DA20	0.70	600	nd	0.79	0.26 ± 0.01	0.45 ± 0.01	0.64	0	0.91 ± 0.02
DA20	0.70	500	3.51	2.52	0.44 ± 0.02	0.13 ± 0.02	0.3 ± 0.03	0	0.75 ± 0.03

na^a - not applicable

nd^b - not detectable

4.4. Conclusions

- (1) SCWG of 5 wt.% glucose-water solution at various temperatures (400-600 °C) showed that methane yield maximized at 500 °C, no significant gasification occurred at 400 °C, while H₂ concentration became the dominant product when the reactor temperature was increased to 600 °C.
- (2) Methane production was more favorable at lower WHSV values, while higher WHSV values caused lower gasification efficiency and a drastic decrease in methane production.
- (3) The Ni_{20%}Ru_{2%}/γ-Al₂O₃ catalyst used in this study showed high activity for SCWG of real aqueous biomass. Almost 0.9 mol/mol of the carbon in the aqueous fraction of pyrolysis oil (2.98 wt.% carbon concentration) was converted into carbon containing gases i.e. CH₄ and CO₂ at 700 °C.
- (4) For the pyrolysis oil aqueous fraction of a lower carbon content (0.71wt.%), this catalyst produced a high carbon gasification efficiency (0.91 mol/mol) even at a lower temperature of 600 °C.
- (5) Methane is the main gas product in SCWG of pyrolysis oil aqueous fraction at 500 °C, but hydrogen dominates in the gas products in all the experiments at >500 °C.
- (6) More carbon deposition was observed with the more concentrated feedstock, as expected, but carbon deposition decreased with increasing the reaction temperatures during the SCWG of the pyrolysis oil aqueous fraction. No tar was observed in the presence of catalyst almost in all experiments.
- (7) Although high concentrations of feedstock may result in deactivation of the catalyst or reactor plugging due to the carbon and tar deposition, this catalyst was found highly stable during 6 hours experiment even using the pyrolysis oil aqueous fraction.
- (8) The ICP analysis results do evidence the possibility of metal (Ni) leaching during the SCWG experiments. A longer reaction time may lead to leaching of the metal catalyst to a larger extent,

which might consequently deactivate the catalysts. As such, seeking catalyst with better resistance to metal leaching would be a focus of the future work

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CHAPTER 5. CONCLUSIONS AND FUTURE WORK

The main contribution of this research was for the successful SCWG of organics present in the aqueous fraction of pyrolysis oil into methane and hydrogen gas using a flow-type reactor. This required optimizing the experimental parameters while also designing an appropriate catalyst to increase the carbon gasification efficiency. Since real aqueous biomass is a complex solution of materials, it was needed to first study SCWG of a model compound. Since the water soluble part of pyrolysis oil consists of high amount of sugar compounds, glucose was chosen as a suitable model compound. In the first part of this study, an innovative heterogeneous $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ catalyst was chosen which demonstrated high activity, stability, and metal dispersion. This catalyst achieved complete carbon gasification and generated ~ 0.5 mol CH_4 /mole of carbon-fed and 0.25 mol H_2 /mol of carbon-fed from SCWG of 5 wt.% glucose-water solution at 500 °C and 27.5 MPa and a WHSV of 3 h⁻¹. No deactivation was observed for this Ni-Ru catalyst during 20 hour on-stream (5 wt.% glucose-water solution, 500 °C and 27.5 MPa). Addition of ruthenium showed the high potential of this metal as a co-catalyst or promoter which improved nickel dispersion, increased catalyst stability, suppressed tar/car formation, and also increased nickel reducibility.

In the second part of this study, it was demonstrated that temperature is the most important factor in the examined SCWG. At $T = 400$ °C, a very small portion of carbon from the glucose model biomass feedstock was converted into gaseous products with the remainder converted into tarry materials or liquid products. Hydrogen production was drastically increased to 0.8 mol/mol of carbon in the feedstock at 600 °C, while methane production gave 0.3 mol/mol of carbon in the feedstock. It should be noted that almost complete carbon gasification efficiency was achieved at 500 °C, so a higher temperature just shifted the gas production toward more hydrogen and carbon dioxide formation, and less methane gas.

The $\text{Ni}_{20\%}\text{Ru}_{2\%}/\gamma\text{-Al}_2\text{O}_3$ catalyst also demonstrated to be very active for the SCWG of an aqueous fraction of pyrolysis oil. The substrate concentration was found to affect the carbon gasification. Since the real aqueous biomass is a more complicated feedstock than glucose, two concentrations of this aqueous phase were prepared based on the carbon content, 0.7 wt.% C and 2.98 wt.% C. Almost 0.9 mol/mol of the carbon in the aqueous fraction of pyrolysis oil (2.98

wt.% carbon concentration) was converted into carbon containing gases i.e. CH₄ and CO₂ at 700 °C. For the pyrolysis oil aqueous fraction of a lower carbon content (0.7 wt.%), this catalyst produced a high gasification efficiency (0.91 mol/mol) even at a lower temperature of 600 °C. Methane is the main gas product in SCWG of pyrolysis oil aqueous fraction at 500 °C, but hydrogen dominates in the gas products in all the experiments at >500 °C. More carbon deposition was observed with the more concentrated feedstock, as expected, but carbon deposition decreased with increasing the reaction temperatures during the SCWG of the pyrolysis oil aqueous fraction. No tar was observed in the presence of catalyst almost in all experiments. Although high concentrations of feedstock may result in deactivation of the catalyst or reactor plugging due to the carbon and tar deposition, this catalyst was found highly stable during 6 hours experiment even using the pyrolysis oil aqueous fraction. The ICP analysis results do evidence the possibility of metal (Ni) leaching during the SCWG experiments. A longer reaction time may lead to leaching of the metal catalyst to a larger extent, which might consequently deactivate the catalysts. As such, seeking catalyst with better resistance to metal leaching would be a focus of the future work.

Future Work and Recommendations

- (1) The catalytic mechanism of the SCWG process needs more investigation. In this study, reusability of catalyst was not examined which should be performed in future works.
- (2) Only two concentrations of aqueous fraction of pyrolysis oil were investigated in this research. Therefore, SCWG of higher concentration of this aqueous biomass should be studied.
- (3) The ICP analysis results do evidence the possibility of metal (Ni) leaching during the SCWG experiments. A longer reaction time may lead to leaching of the metal catalyst to a larger extent, which might consequently deactivate the catalysts. As such, seeking catalyst with better resistance to metal leaching would be a focus of the future work.
- (4) Effect of alkali elements in real aqueous biomass were not investigated in this study. Hence, future studies should focus on how these elements can promote either methane or hydrogen production.

(5) Only 2 wt.% of ruthenium was used in Ni-Ru catalyst. Therefore, various Ru-to-Ni molar ratios should be examined to better understand the mechanisms on how Ru promotes the stability of the γ -Al₂O₃, and also how this metal enhances the nickel dispersion.

(6) All the catalysts were prepared in one specific size in this study. However, the influence of various catalyst particle sizes on gas yields can be investigated in the future works.

(7) Although the Ni-Ru catalyst in this study was highly stable for 20 hour, future studies should focus on longer time experiments within days and hours to find out the catalyst life time.


(8) SCWG of only one type of biomass was studied in the presence of the Ni-Ru catalyst in this study, but influence of this catalyst could be investigated for other type of biomass.

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Publication: Industrial & Engineering Chemistry Research

Publisher: American Chemical Society

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